FINAL REPORT ON THE RESULTS FROM THE POKER FLAT, DENALI NATIONAL PARK AND PRESERVE, AND TRAPPER CREEK CASTNET PROTOCOL SITES JULY 1998 THROUGH JUNE 2001

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September 2003

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Executive Summary

This report was prepared by Air Resource Specialists, Inc. (ARS), to summarize three years (July 1998 – June 2001) of ambient chemical concentration and meteorology data collected at three sites in Interior Alaska.

This monitoring program resulted from negotiations that occurred during permitting for the Healy Clean Coal Project, a coal fired power plant located four miles from Denali National Park and Preserve. The objective of the program was to compare ambient air quality at the northeast corner of Denali National Park and Preserve against regional conditions. Source apportionment was not in the scope of this study.

Three sites were installed in Interior Alaska to collect chemical concentration and meteorological data; Poker Flat, Denali National Park and Preserve (Denali), and Trapper Creek.

Ambient chemical concentration data was collected using a three-stage filter pack designed for the Environmental Protection Agency's Clean Air Status and Trends Network (CASTNet) program. This method collects particles and selected gases by passing ambient air through a sequence of Teflon®, nylon, and Whatman filters. Filters were exposed for one week, Tuesday to Tuesday. The following chemical species were collected and analyzed directly or indirectly: particulate sulfate (p-SO_4^{2-}), sulfur dioxide (SO_2), particulate nitrate (p-NO_3^{1-}), nitric acid (HNO_3), and ammonium (NH_4^{1+}).

Meteorological sensors monitored temperature, wind speed and wind direction at 10 meters above ground level. Data collection and validation were conducted in accordance with EPA guidelines (EPA Quality Assurance Handbook for Air Pollution Measurement Systems, Volume IV: Section 4.0 - 4.2).

Regional Sources

Fossil-fuel combustion and industrial processes are the primary sources of particulate sulfate, sulfur dioxide, and nitrogen oxides (which produce particulate nitrate and nitric acid though oxidation). Agriculture is the primary source of ammonium. In Alaska, there are few large fossil-fuel combustion sources and limited industry and agriculture in comparison to the lower 48 states. The stationary fossil-fuel combustion source closest to Denali National Park and Preserve is the Healy Power Generating Station. This power station has two coal-fired units: Unit 1 and the Healy Clean Coal Project (HCCP). Unit 1 operated during the entire three-year monitoring period. HCCP shut down half way through the monitoring period in December 1999.

The biomass burning in Alaska consists primarily of wildfires during the summer and wood smoke from fireplaces and wood-burning stoves during the winter. Emissions of this type are dominated by organic and elemental carbon compounds and potassium (Watson and Chow, 1994; Turn *et al*., 1997). However, the fires also release nitrate, ammonium, sulfate, and other compounds as a small percentage of the overall emissions (Seinfeld and Pandis, 1998).

During winter in Alaska, the ground is covered with snow, there are few lightning storms, and the northern oceans are covered with ice. This decreases the pollutant emissions due to oceans, lightning, vegetation, and soils during the winter months. Since sulfur dioxide converts to sulfate through photochemical or aqueous chemistry mechanisms, both of which are greatly reduced or non-existent during winter in Alaska, the sulfur dioxide to sulfate conversion should be minimal during winter (Seinfeld and Pandis, 1998).

Arctic haze, the layered haze bands of Northern European and Russian anthropogenic emissions that travel around the Arctic and into Alaska during winter, is one of the predominant influences on Alaskan air quality during winter. It is primarily composed of sulfur compounds and soot, but also contains a variety of metals such as lead, nickel, copper, cadmium, vanadium, manganese as well as other elemental compounds such as arsenic, nitrate, sodium, etc. (Barrie *et al.*, 1989; Shaw and Khalil, 1989). The transport of these emissions from their sources in Northern Europe and Russia into Alaska during winter is well documented (Rahn and Shaw, 1982; Shaw and Khalil, 1989).

Data Summary

The annual variability of the meteorology and chemical component concentrations at the three sites is significantly high. Any further studies must be designed for multiple years to account for this variability.

Meteorological

Poker Flat Air Flow

Air flow in the Poker Flat area is very seasonal and typical of the Alaska interior. The region experiences cold, dry northerly air flow in the winter months and southerly air flow from the Gulf of Alaska in the summer. During the July to August periods the winds were primarily out of the west-southwest to southwest. During the month of September the winds transitioned from west-southwest to east-northeast. During the Fall/Winter seasons (October to March) the winds were primarily out of the east-northeast. April was a month of transitioning from east-northeast back to west-southwest. The winds from May to June were back to the summer air flow pattern of west-southwest to southwest. The Poker Flat station is in the Chatanika River drainage and the winds are heavily influenced by the orientation of the valley, west-southwest to east-northeast.

Denali National Park and Preserve Air Flow

Air flow in the Denali National Park site is complex. Complex topographic features of the local area affect northerly winter flow and southerly summer flow, so typical to the region. The site is in mountainous terrain of the Alaska Range. The Nenana River flows south to north in a deep canyon. Mountains surround the site in all directions. As a result, the winds do not favor particular directions and no seasonal trends were observed with this data.

Trapper Creek Air Flow

Air flow in the Trapper Creek area is predominately north or south, depending on the season, because of the orientation of the Susitna River valley. During the July to August periods the winds were mixed with directions out of the north or south equally. September was a month of transitioning from equal northerly and southerly winds to mostly northerly. During the Fall/Winter season (October to March) the winds were primarily out of the north. April was a transition month which saw winds begin to switch to southerly. May and June saw the cycle complete with equally mixed northerly and southerly winds.

Chemical

Particulate Sulfate

Sulfate appears to be regional in nature and primarily of the form of ammonium sulfate although periods of ammonium bisulfate occur, especially during winter. Sulfate concentrations are usually highest in the winter/spring (~ 0.1-1.0μg m^{-3}) and lowest in the summer/fall (~ 0.05-0.3μg m^{-3}) seasons. Arctic haze may be responsible for the majority of the sulfate observed during the winter.

Sulfur Dioxide

Sulfur dioxide shows the strongest seasonal variability of the components included in this study. During the spring, summer and early fall seasons (April through October) sulfur dioxide concentrations are consistently low at Denali and Poker Flat. During the mid-fall and winter seasons (November through March), sulfur dioxide concentrations are consistently higher than summer values at Denali and Poker Flat.

During the first two winters, Denali and Poker Flat appear to be influenced by regional sources of sulfur dioxide, and during all three winters, there is a source of sulfur dioxide that causes the Denali concentrations to be above regional background values.

The sulfur dioxide concentrations at Trapper Creek remain low (~ 0.1-0.2μg m^{-3}) for the entire three year study.

Particulate Nitrate

Particulate nitrate concentrations are generally higher at Trapper Creek than at Poker Flat and Denali, but on average remain low (< 0.1μg m^{-3} for Poker Flat and Denali and < 0.2μg m^{-3} for Trapper Creek).

Nitric Acid

Nitric acid concentrations are generally higher at Poker Flat than at Denali and Trapper Creek.

Ammonium

Particulate ammonium concentrations are usually low (between 0.02 and 0.2μg m^{-3}). Ammonium reaches its maximum during the spring/summer months when biological activity is high.

Correlations Between Sites

Comparisons were made for each component between each site and the R^2 values were calculated. The R^2 value is a measure of the relationship between two variables. An R^2 value of 1 indicates a perfect correlation between the two variables while an R^2 value of 0 indicates no correlation between the two variables.

There was a high degree of variability seen in the between site comparisons. This variability can be due to a number of factors which include values near the minimum detectable limits and local meteorological conditions (wind direction, wind speed, temperature and relative humidity). The following observations were made from the between site comparisons:

- Sulfate usually correlates well ($R^2 > 0.50$) between all sites in the summer and winter seasons, the two more regional transport periods.
- Good correlations for sulfur dioxide are seen between Poker Flat and Denali and Trapper Creek and Denali, but they vary by season and year.
- Good correlations for particulate nitrate are seen between Poker Flat and Denali, but they vary by season and year.
- Nitric acid usually correlates well between all sites during the warmer periods, spring/summer seasons, and poorly during the colder periods, fall/winter seasons.
- Ammonium usually correlates well between sites during the summer season, but has large inter-annual variability during the other seasons.

Correlations Between Chemical Components

Comparisons were made for each site between each component and the R^2 values were calculated.

There was a high degree of variability seen in the between component comparisons. This variability can be due to a number of factors which include values near the minimum detectable limits, differing emission sources and meteorology (wind direction, wind speed, temperature and relative humidity). The following observations were made from the between component comparisons:

- Sulfate and Ammonium demonstrated good correlations for almost all seasons at all sites, with the exception of Poker Flat during Year 1 of the study.
- Poor correlations are predominantly seen at all sites for all seasons between sulfur dioxide and sulfate.
- Poor correlations between ammonium and sulfur dioxide are seen at all sites for all seasons.
- Poor correlations are predominantly seen at all sites for all seasons between ammonium and particulate nitrate.
- Poor correlations between particulate nitrate and nitric acid are seen at all sites for almost every season.
- The remainder of the between component correlations varied significantly by site and by year.

National Standards

In the context of air quality across the United States, these sites are very clean.

- According to the Interagency Monitoring of Protected Visual Environments (IMPROVE) network, the annual average concentration of fine mass at Denali National Park and Preserve was 1.4μg m^{-3} between 1996 and 1998 (http://vista.cira.colostate.edu/improve/Data/GraphicViewer/seasonal.htm). It is the lowest annual average fine mass concentration in the IMPROVE network during this period. However, despite Denali's clean air, the chemical components reaching Denali show that Denali is experiencing the effects of international transport, such as sulfur compounds brought in during Arctic Haze episodes.
- The National Ambient Air Quality Standard (NAAQS) for annual average fine mass is 15μg m^{-3} so Denali's weekly fine mass is less than one tenth of the annual NAAQS for fine mass.
- The NAAQS for sulfur dioxide is an annual arithmetic mean of 0.03 ppm or ~ 80μg m^{-3} (http://www.epa.gov/airs/criteria.html) so Denali's highest, weekly-averaged, sulfur dioxide concentration of 3.10μg m^{-3} is far below the annual NAAQS for sulfur dioxide.

1.0 INTRODUCTION

In July 1998, three sites were established in Interior Alaska to measure ambient chemical concentrations (atmospheric sulfur and nitrogen compounds) and meteorology for a period of three years. The monitoring program resulted from negotiations that occurred during permitting for the Healy Clean Coal Project, a coal-fired power plant located four miles from Denali National Park and Preserve. The objective of the program was to compare ambient air quality at the northeast corner of Denali National Park and Preserve against regional conditions. Source apportionment was not in the scope of this study. Monitoring site locations are shown in Figures 1-1 through 1-4. Instrument configurations at each site are presented in Appendix A. Project participants and their roles in the monitoring effort include:

• National Park Foundation (NPF)	Contract Administrator
• National Park Service (NPS)	Technical Director
• Air Resource Specialists, Inc. (ARS)	Primary Contractor
• Alaska Industrial Development and Export Authority (AIDEA)	Technical Reviewer
• Golden Valley Electric Association (GVEA)	Technical Reviewer
• Trustees for Alaska	Technical Reviewer
• C.F. Cahill, University of Alaska	Consultant

Sampling methods followed those established by the Environmental Protection Agency's Clean Air Status and Trends Network (CASTNet) steering committee. The CASTNet program, formerly known as the National Dry Deposition Network, was established in 1987 to measure dry deposition of atmospheric sulfur and nitrogen compounds. The CASTNet program operates over 70 monitoring stations in the U.S., but there were no sites in Alaska until this three-year monitoring effort began.

Ambient chemical concentration data was collected by drawing ambient air through specially prepared filters. The filters were exposed for one week, Tuesday to Tuesday, at a height of 10 meters above ground level. Exposed filters were shipped to the contracting laboratory for chemical analysis. The concentrations were calculated by dividing the component mass by the total volume of air sampled at EPA standard conditions (25°C and 760 mmHg). This monitoring program collected and analyzed directly or indirectly five chemical species: particulate sulfate (p-SO_4^{2-}), sulfur dioxide (SO_2), particulate nitrate (p-NO_3^{1-}), nitric acid (HNO_3), and ammonium (NH_4^{1+}).

Meteorological sensors monitored temperature, wind speed, and wind direction at 10 meters above ground level. Temperature and wind data were collected with on-site data loggers and the data were retrieved periodically by ARS. The chemical concentrations and meteorological data were compiled by ARS in a database. The data were analyzed, summarized, and compared among the three sites.

This report covers the entire sampling period (July 1998 to June 2001). All work performed during the three-year study period is described in this report. An interim report, *First-Year Report on the Results from the Poker Flat, Denali National Park and Preserve, and Trapper Creek, July 1998 through June 1999*, was released in July 2000. This interim report is available upon request from Air Resource Specialists, Inc.

The views and conclusions contained in this document are those of the authors and should not be interpreted as representing the options or policies of the U.S. Government. Mention of trade names or commercial products does not constitute their endorsement by the U.S. Government.

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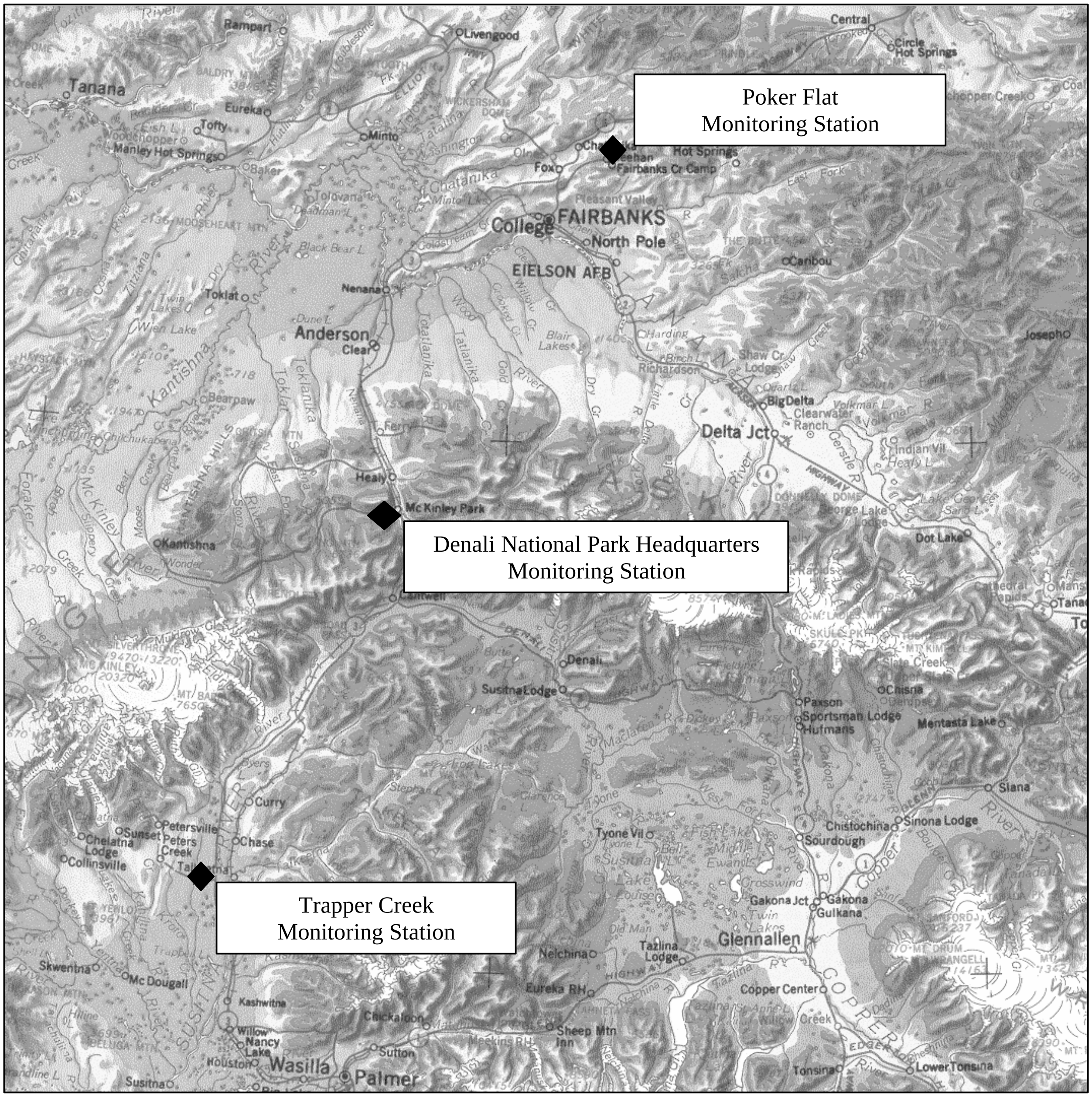
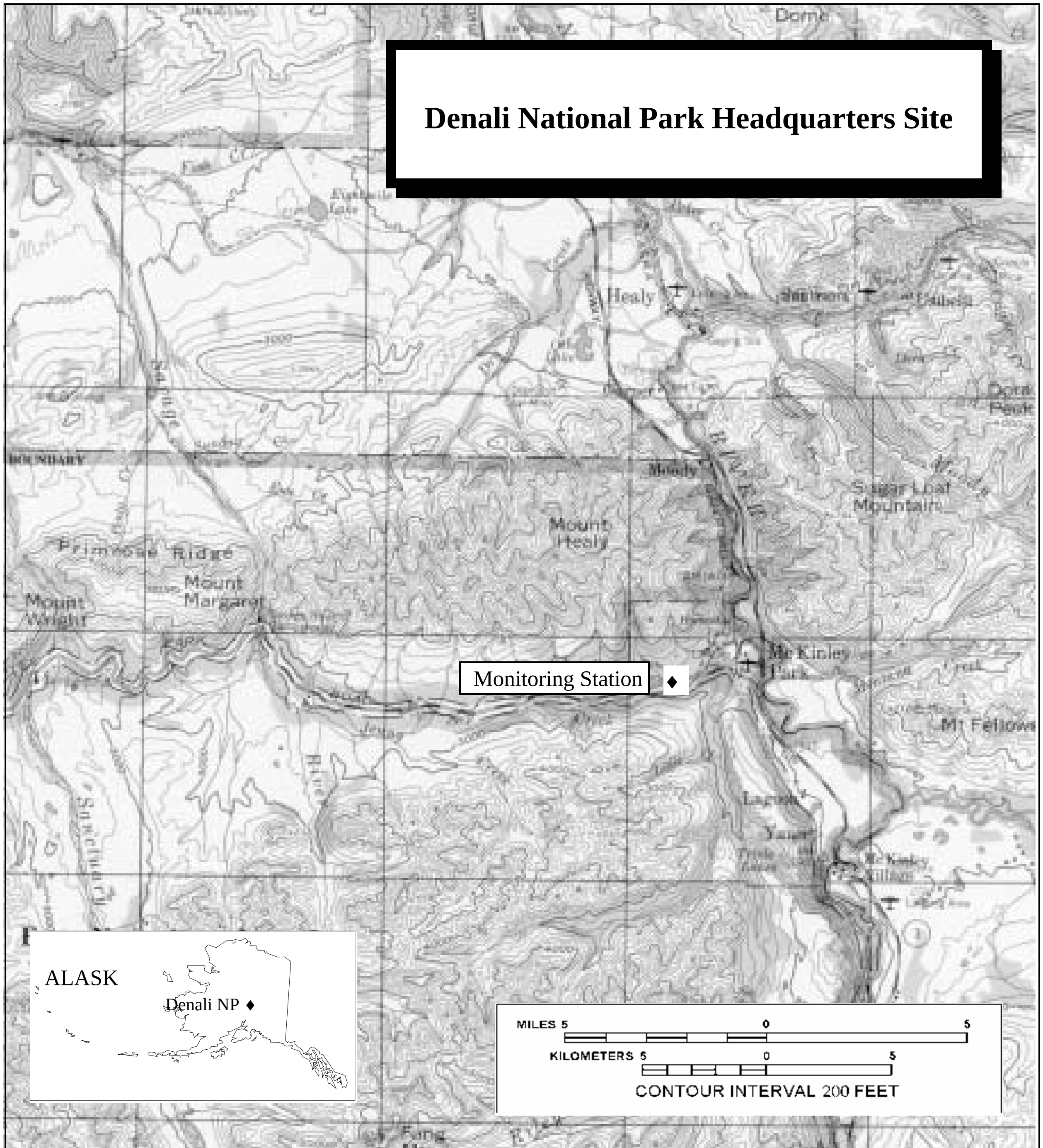


Figure 1-1 Monitoring site locations for Poker Flat, Denali National Park and Preserve, and Trapper Creek.

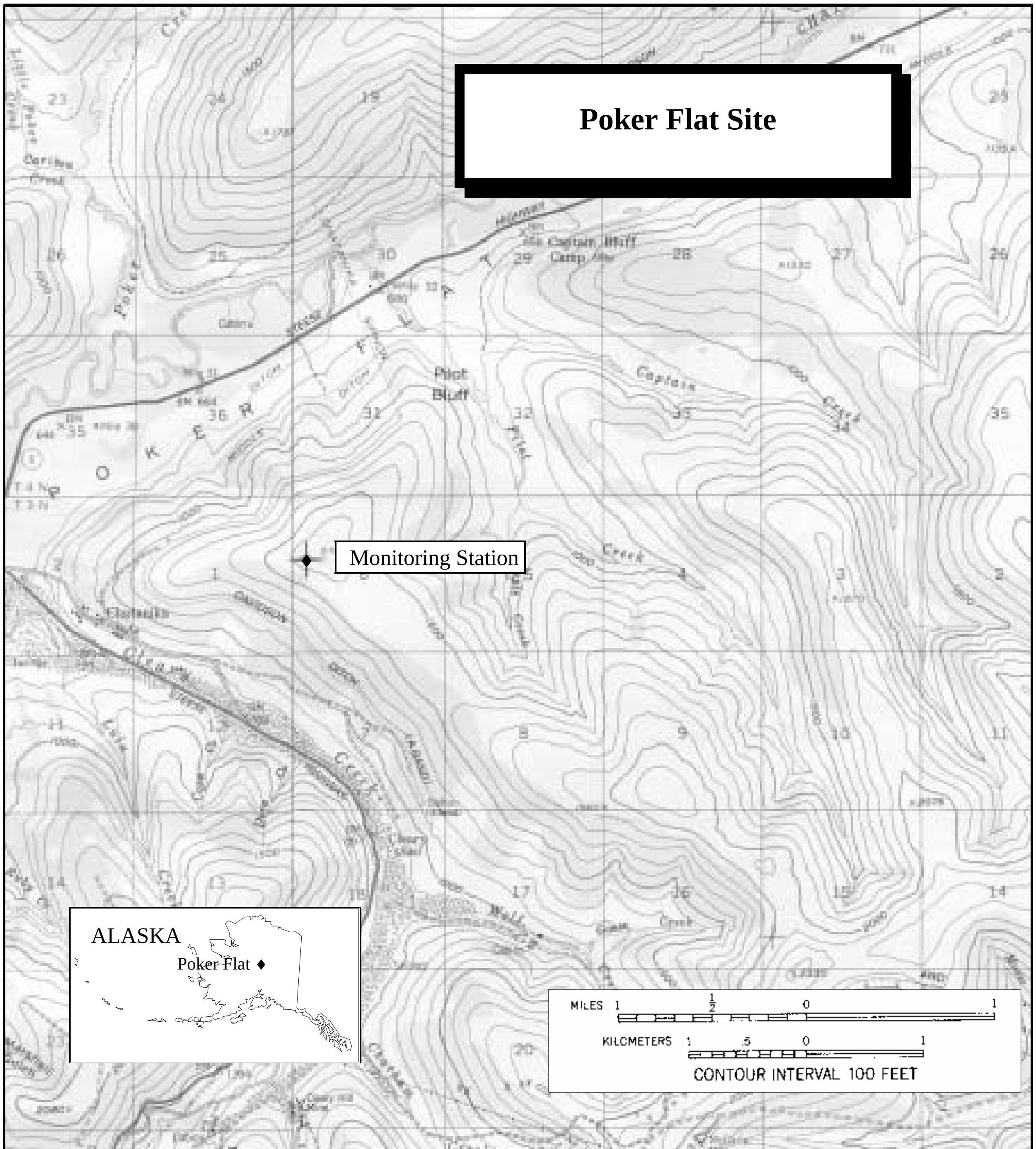


SITE IDENTIFICATION	
Site Abbreviation:	DENA

INSTRUMENTATION	
Wind Speed	Temperature
Wind Direction	
Filter Pack Flow	

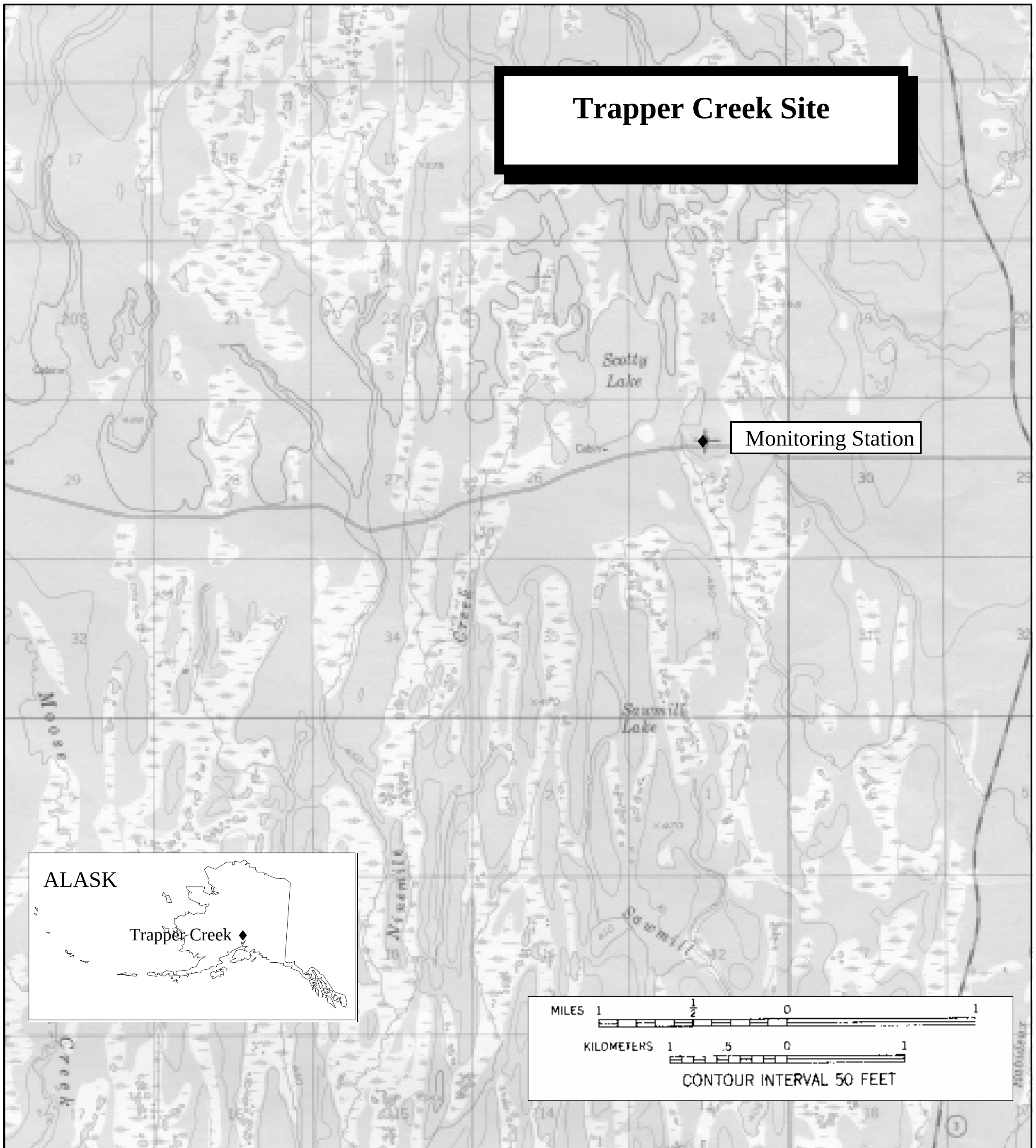
MAP INFORMATION	
Mean Elevation:	661 m
Longitude:	148° 57' 48"W
Latitude:	63° 43' 33"N
UTM Zone:	6
Easting:	403040 m
Northing:	7067751 m
Map Reference:	Healy N6300-W4700/ l:250,000

Figure 1-2. Location of Denali National Park and Preserve monitoring site.



SITE IDENTIFICATION		MAP INFORMATION	
Site Abbreviation:	DENA-PF	Mean Elevation:	495m
		Longitude:	147º 26' 00" W
		Latitude:	65º 07' 04" N
		UTM Zone:	6
Filter Pack Flow	Wind Direction	Easting:	479654m
Temperature		Northing:	7221457m
Wind Speed		Map Reference:	Livengood, AK 1:63,360

Figure 1-3. Location of Poker Flat monitoring site.



SITE IDENTIFICATION		MAP INFORMATION	
Site Abbreviation:	DENA-TC	Mean Elevation:	116 MSL
		Longitude:	150º 18' 02" W
		Latitude:	62º 19' 06" N
		UTM Zone:	5
Filter Pack Flow	Wind Direction	Easting:	639888 m
Temperature		Northing:	6912361 m
Wind Speed		Map Reference:	Talkeetna, AK 1:63,360

Figure 1-4. Location of Trapper Creek monitoring site.

2.0 EXPERIMENTAL METHODS

2.1 AMBIENT CHEMICAL CONCENTRATIONS

The sampling for sulfur and nitrogen species used a three-stage filter pack designed for the EPA's CASTNet program. This method collected particles and selected gases by passing ambient air through a sequence of Teflon®, nylon, and Whatman filters. The Teflon® filter removed the SO_4, NO_3, and NH_4. The nylon filter removed HNO_3 and reacted with SO_2 gas to form SO_4. The Whatman filter had a cellulose fiber base, impregnated with potassium carbonate (K_2CO_3) and was also used for removal of SO_2 gas. The nylon filter SO_2 and the Whatman filter SO_2 were summed to provide weekly average SO_2 concentrations.

Each filter sampled ambient air from a height of 10 meters above the ground at a constant mass flow controlled rate of 3.00 liters per minute for a period of one week. The filter handling, analysis, and data collection for this project included the following:

- Filter pack cassettes were prepared by the ESE laboratory in Gainesville, Florida. ESE is the current contractor for the CASTNet program. ESE then mailed the filters to the site operators.

- The site operator removed the exposed filter packs between 0900 and 1200 local standard time each Tuesday. Flow data stored on the onsite data loggers were downloaded by the operator and emailed to ARS. The operator also completed forms that included additional information needed to calculate pollutant concentrations and ensure that the data were collected in a manner consistent with the CASTNet program. The exposed filters and forms were mailed by the operator to ESE. A new unexposed filter was installed during the operator's site visit and a new week of sampling began.

- Filters were received at ESE and underwent chemical analysis in the laboratory. The analytical process yielded total mass of all components.

- The data were sent to ARS where they were entered into the database for quality assurance screening and calculation of the weekly concentration for all components.

2.2 METEOROLOGICAL DATA

The data collection and validation were conducted in accordance with EPA guidelines (EPA Quality Assurance Handbook for Air Pollution Measurement Systems, Volume IV: Section 4.0 - 4.2).

The wind sensor at each site was installed on a tower at a height of 10 meters. The wind signals were received, processed, and stored by a data logger. The scalar wind speed, vector wind direction, and standard deviation of wind direction hourly averages were downloaded by the site operator and electronically transferred by Air Resource Specialists, Inc. (ARS).

The ambient temperature sensors were installed on each tower at about 9 meters. The signals were processed similarly to the winds. The temperature data were not used in this report.

Once at ARS the data were loaded into a database and screened for anomalies. Problems such as missing data and out of range values were addressed immediately. The data were validated monthly using automatic screening and graphic review. Valid data were processed and reported by a rose plot program.

All three sites utilized a 10-meter aluminum fold-down tower manufactured by the same supplier used in the CASTNet program. Whenever possible, the measurement and collection instrumentation that was selected by the CASTNet program was also selected for this program. At the top of the tower the wind sensor was mounted and oriented to true north. Wind speed and wind direction are measured from 10 meters above ground level.

Signals from each sensor were collected, scaled, and stored by the site’s data logger. In addition, the standard deviation of the wind direction was calculated and stored. Other parameters, such as data logger battery voltage and site shelter temperature, were collected for use in diagnostics.

3.0 BACKGROUND

This section describes the primary source types of the atmospheric pollutants measured during this study, the chemical transformations that can cause the pollutants to convert to other forms, and the regional sources in the study area.

It should be noted that the objective of this study was to compare ambient air quality at the northeast corner of Denali National Park and Preserve against regional conditions. Source apportionment was not in the scope of this study.

3.1 PRIMARY SOURCE TYPES

The primary sources of the atmospheric pollutants measured in this study are:

Pollutant	Source
Particulate Sulfate	Fossil-fuel combustion and industrial processes Biomass burning Oceans Plants and Soils Volcanoes
Sulfur Dioxide	Fossil-fuel combustion and industrial processes Biomass burning Volcanoes
Particulate Nitrate	Oxidation of nitrogen oxides – sources of nitrogen oxides include: Fossil-fuel combustion Soil release Biomass burning Lightning Ammonia oxidation Aircraft and transport from the stratosphere
Nitric Acid	Oxidation of nitrogen oxides (specifically nitrogen dioxide and to a lesser extent nitrate)
Ammonium	Ammonia from agricultural and other biological sources including: Dairy cattle, beef cattle, buffalo, pigs, horses, sheep, goats, poultry Wild Animals Fertilizer Biomass burning Vegetation Oceans (Seinfeld and Pandis, 1998)

3.2 CONVERSION

Once the sources emit the primary compounds into the atmosphere, chemical transformations can cause the compounds to convert to other forms. Sulfur dioxide is converted to sulfate through atmospheric reactions with the hydroxyl radical (OH), which is produced by photochemical reactions (i.e. chemical reactions fueled by sunlight), and aqueous chemical reactions (i.e. reactions that occur inside water droplets).

The ammonia gas present in the atmosphere can react, in the presence of water, with sulfur compounds to form ammonium sulfate, $(NH_4)_2SO_4$, or ammonium bisulfate, NH_4HSO_4. The resulting sulfate compounds will depend on the availability of ammonia gas. Ammonium sulfate results if ammonia is not limited. If ammonia is limited, ammonium bisulfate will form. If there is no ammonia present, the sulfate can be in the form of pure sulfuric acid (Seinfeld and Pandis, 1998).

The concentration of particulate nitrate, primarily in the form of ammonium nitrate, NH_4NO_3, is dependent on the concentrations of nitric acid and ammonia in the atmosphere. Chemically, there is an equilibrium between gaseous nitric acid and ammonia and particulate ammonium nitrate, so the amount of particulate ammonium nitrate depends on the amount of ammonia and nitric acid available for reaction. The term particulate nitrate used in this report includes both the solid and aqueous forms of ammonium nitrate. However, the dynamics of the ammonium nitrate vary with relative humidity. Above the deliquescence point, the point at which the atmospheric relative humidity is high enough that the ammonium nitrate can attract water molecules, dissolve and become and aqueous solution (i.e. a liquid), the ammonium nitrate exists in an aqueous form; below the deliquescence point, the ammonium nitrate is a solid. However, the solid ammonium nitrate is more likely to volatize than the liquid. This volatilization is temperature dependent; as the temperature increases, the compound volatizes more readily (Seinfeld and Pandis, 1998).

Sulfate-nitrate-ammonia chemistry is complex and the relative amounts and types of sulfate and nitrate compounds depend on the availability of each in the atmosphere and the temperature and the relative humidity. In the absence of available sulfate or nitrate, ammonia will remain gaseous.

3.3 REGIONAL SOURCES

In Alaska, there are few large fossil-fuel combustion sources and limited industry and agriculture in comparison to the lower 48 states. The stationary fossil-fuel combustion source closest to Denali National Park and Preserve is the Healy Power Generating Station. This power station has two units: Unit 1 and the Healy Clean Coal Project (HCCP). Unit 1, a 25 MW unit, operated during the entire three-year monitoring period. HCCP, a 50 MW unit, shut down half way through the monitoring period in December 1999.

The biomass burning in Alaska consists primarily of wildfires during the summer and wood smoke from fireplaces and wood-burning stoves during the winter. In summer, wildfires emit large amounts of aerosols into the Alaskan atmosphere. These emissions are dominated by organic and elemental carbon compounds and potassium (Watson and Chow, 1994; Turn *et al.*, 1997). However, the fires also release nitrate, ammonium, sulfate, and other compounds as a small percentage of the overall emissions (Seinfeld and Pandis, 1998). Wood smoke from fireplaces and wood-burning stoves will provide the same carbon and potassium signatures as wildfires, but will occur during the winter.

During winter in Alaska, the ground is covered with snow, there are few lightning storms, and the northern oceans are covered with ice. This decreases the pollutant emissions due to oceans, lightning, vegetation, and soils during the winter months. Since sulfur dioxide converts to sulfate through photochemical or aqueous chemistry mechanisms, both of which are greatly reduced or non-existent during winter in Alaska, the sulfur dioxide to sulfate conversion should be minimal during winter (Seinfeld and Pandis, 1998).

Arctic haze, the layered haze bands of Northern European and Russian anthropogenic emissions that travel around the Arctic and into Alaska during winter, is one of the predominant influences on Alaskan air quality during winter. It is primarily composed of sulfur compounds and soot, but also contains a variety of metals such as lead, nickel, copper, cadmium, vanadium, manganese as well as other elemental compounds such as arsenic, nitrate, sodium, etc. (Barrie *et al.*, 1989; Shaw and Khalil, 1989). The transport of these emissions from their sources in Northern Europe and Russia into Alaska during winter is well documented (Rahn and Shaw, 1982; Shaw and Khalil, 1989).

4.0 RESULTS

4.1 CHEMICAL AIR QUALITY DATA

This section presents the chemical concentration results for Poker Flat, Denali National Park and Preserve, and Trapper Creek. These data were compiled from the analyses of filters collected at each of the three study sites for the entire sampling period (July 1998 through June 2001). The filter pack analyses yielded weekly average concentrations of particulate sulfate (p-SO_4^{2-}), sulfur dioxide (SO_2), particulate nitrate (p-NO_3^{1-}), nitric acid (HNO_3), and particulate ammonium (NH_4^{1+}).

The chemical concentration data in this section is displayed as component time series, comparisons are made between sites for each component and between components for each site, and comparisons are made to national air quality standards.

4.1.1 Component Time Series

Figures 4-1 through 4-5 show time-series of particulate sulfate, sulfur dioxide, particulate nitrate, gaseous nitric acid, and particulate ammonium at Poker Flat, Denali National Park and Preserve (Denali), and Trapper Creek.

Sulfate

Figure 4-1 demonstrates the following:

- Sulfate appears to be regional, causing all three sites to reach peaks simultaneously.
- The highest sulfate concentrations are usually seen at Poker Flat or Trapper Creek, with Denali's sulfate concentration falling between the two.
- For all three sites, sulfate concentrations are usually lowest (~ 0.05-0.3µg m^{-3}) mid-summer to fall, but the length of the period of low concentrations varies greatly from year to year.
- At all three sites during all three years, a period of elevated sulfate concentrations starts during the winter and continues into the middle of summer.
- Sulfate concentrations at the three sites, for all three years show an increase in fall/winter. These fall/winter increases are consistent with the onset of Arctic haze.

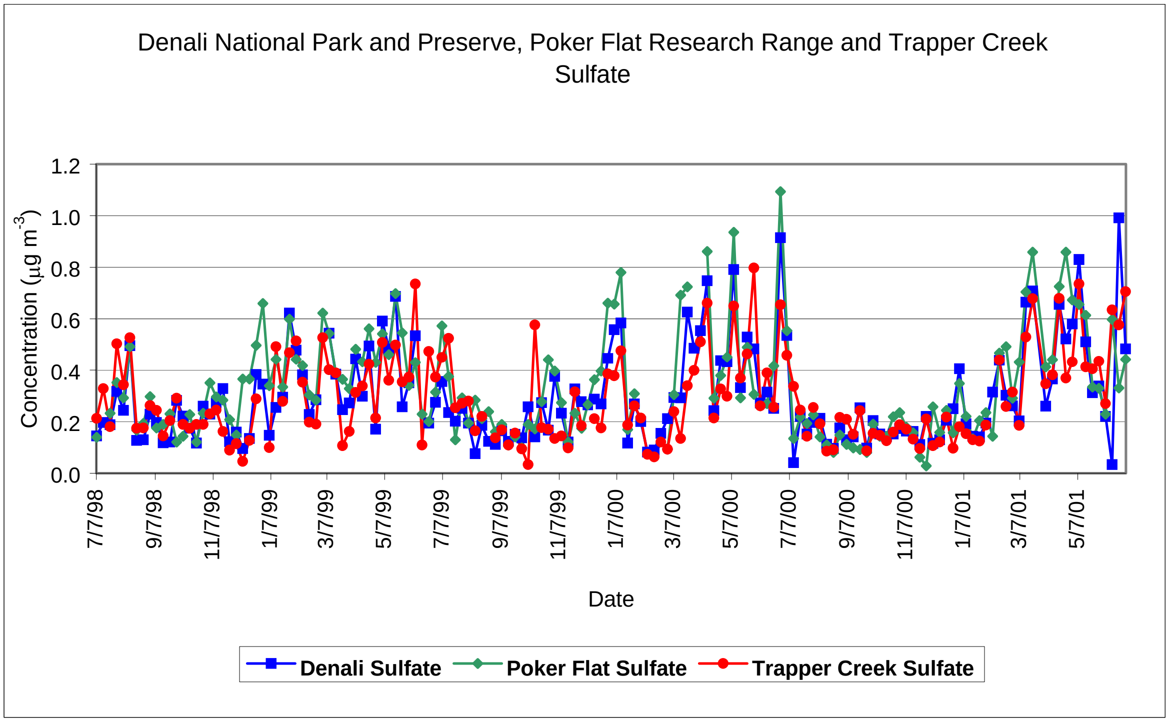


Figure 4-1. Sulfate at Poker Flat, Denali National Park and Preserve, and Trapper Creek, July 1998 to June 2001.

Sulfur Dioxide

Figure 4-2 demonstrates the following:

- Sulfur dioxide shows the strongest seasonal variability of the components included in this study. During the spring, summer and early fall seasons (April through October) sulfur dioxide concentrations are consistently low at all three sites. During the mid-fall and winter seasons (November through March), sulfur dioxide concentrations are consistently higher than summer values at Denali and Poker Flat.
- Occasionally sulfur dioxide peaks at Trapper Creek correspond to large peaks at Denali and Poker Flat. An example of this can be seen during the week of January 26, 1999. These peaks are believed to be regional in nature and consistent with Arctic haze.
- In the first two fall/winters, Denali and Poker Flat appear to be influenced by regional sources of sulfur dioxide, and during all three winters there is a source of sulfur dioxide that causes the Denali concentrations to be above regional background values.

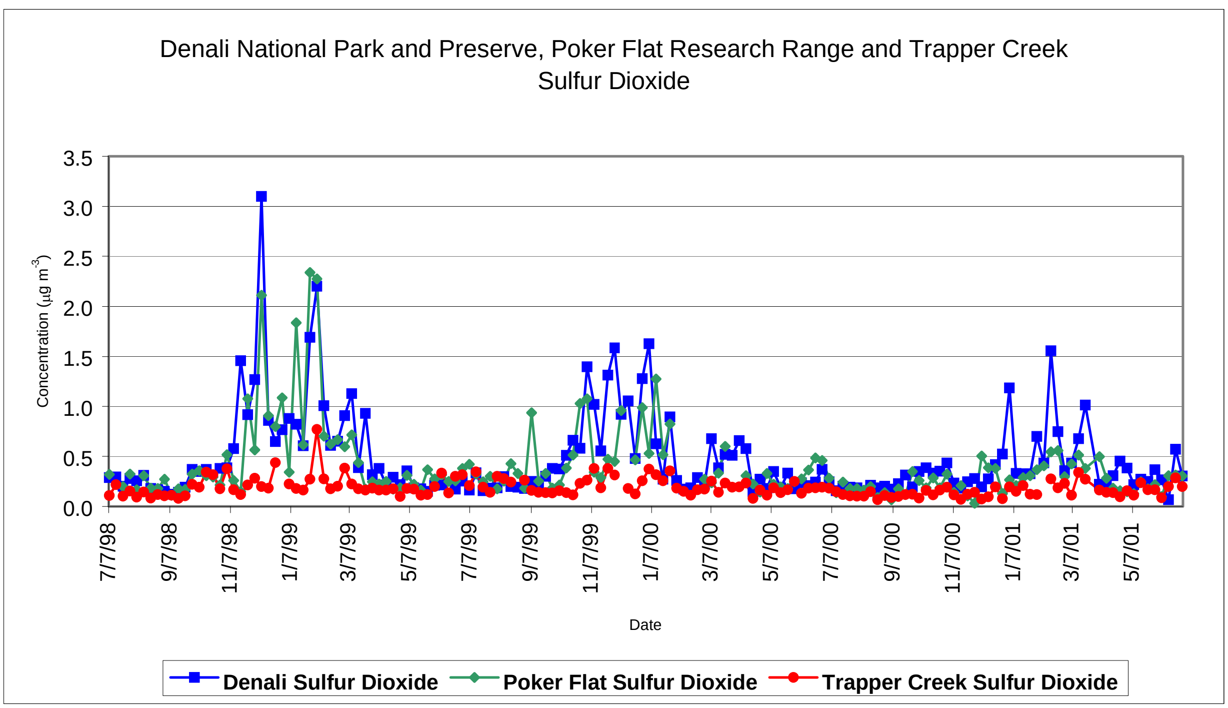


Figure 4-2. Sulfur Dioxide at Poker Flat, Denali National Park and Preserve, and Trapper Creek, July 1998 to June 2001.

Particulate Nitrate

Figure 4-3 demonstrates the following:

- In contrast to sulfate and sulfur dioxide, the particulate nitrate, on average, remains low (< 0.1µg m^{-3} for Poker Flat and Denali and < 0.2µg m^{-3} for Trapper Creek) throughout the year.
- Particulate nitrate concentrations are generally higher at Trapper Creek than at Poker Flat and Denali.
- The three highest particulate nitrate peaks (December 8, 1998, January 26, 1999, and June 23, 2000) were seen simultaneously at all three sites. During these peaks, Poker Flat had the highest concentrations. These peaks appear to be regional in nature, but each peak has different characteristics.
    - During the December peak, the particulate nitrate, sulfate, and sulfur dioxide are high, while the nitric acid and ammonium are low at all three sites. This may indicate artic haze.
    - The January peak corresponds to high sulfur dioxide concentrations at Poker Flat and Denali. During this peak, the concentrations of ammonium, sulfate, and nitric acid are low at all three sites, although the concentrations of sulfate and nitric acid are slightly elevated at Poker Flat. This may indicate artic haze without the sulfate signature.
    - During the June peak, the particulate nitrate, sulfate, ammonium, nitric acid, and sulfur dioxide concentrations are high at all three sites, which may indicate wildfire smoke.

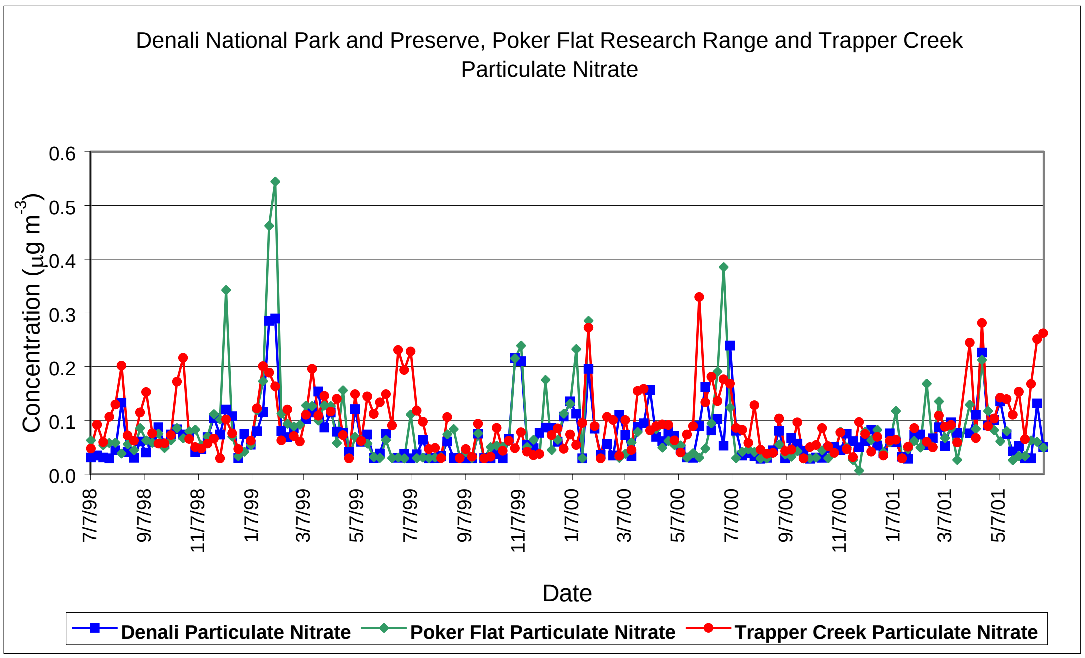


Figure 4-3. Particulate Nitrate at Poker Flat, Denali National Park and Preserve, and Trapper Creek, July 1998 to June 2001.

Nitric Acid

Figure 4-4 demonstrates the following:

- Nitric acid shows a strong seasonal variability, especially at Poker Flat.
  - Poker Flat experiences many nitric acid concentration peaks in winter and summer.
  - Trapper Creek, with the exception of the peaks in fall 1998, usually only experiences elevated nitric acid concentrations in spring/summer (May to July).
  - Denali's nitric acid concentrations are usually elevated when either Trapper Creek or Poker Flat shows a peak, but the concentrations are much lower in magnitude than the peaks at the other sites. This indicates that the nitric acid concentrations appear to be regional.

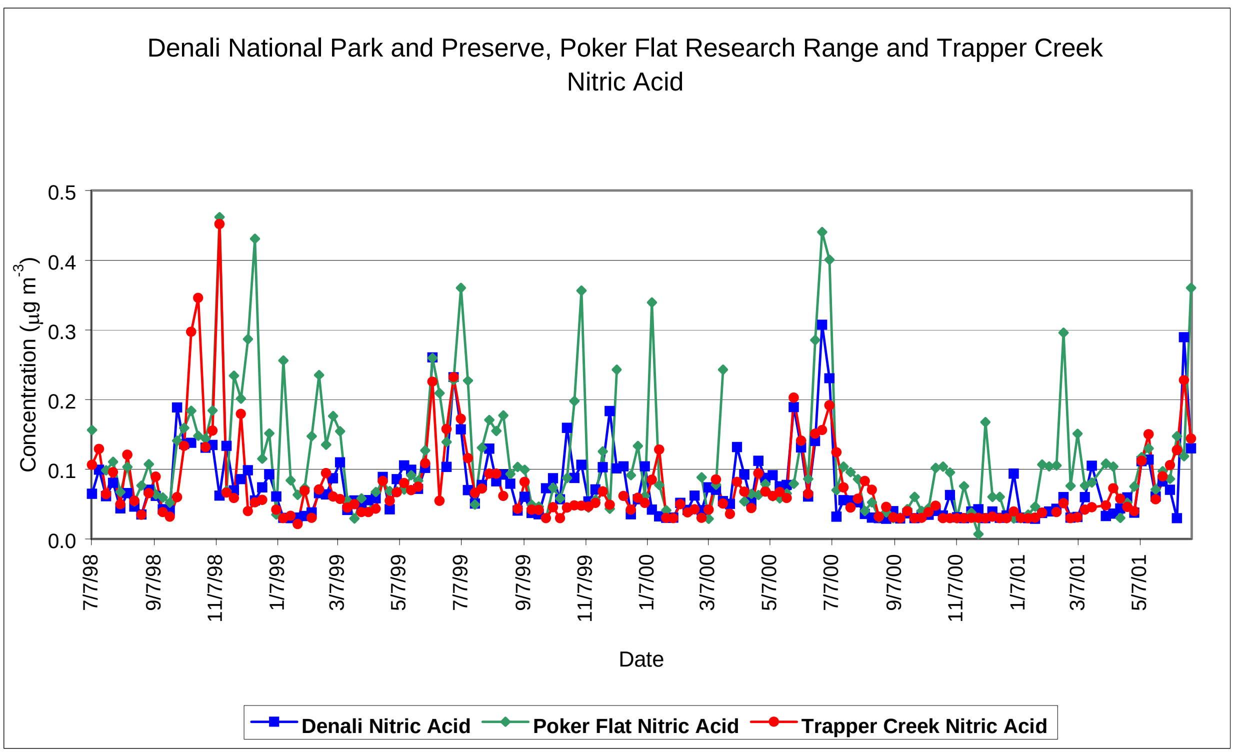


Figure 4-4. Nitric Acid at Poker Flat, Denali National Park and Preserve, and Trapper Creek, July 1998 to June 2001.

Particulate Ammonium

Figure 4-5 demonstrates the following:

- Particulate ammonium concentrations are usually low (falling between 0.02 and 0.2µg m^{-3}).
- The highest ammonium concentration (0.67µg m^{-3}) observed during the study occurred at Poker Flat during the week of June 23, 2000.
- Particulate ammonium concentrations usually follow the sulfate concentration pattern (Figure 4-1). This is to be expected as most sulfate in the atmosphere is in the form of ammonium sulfate or ammonium bisulfate (Seinfeld and Pandis, 1998).

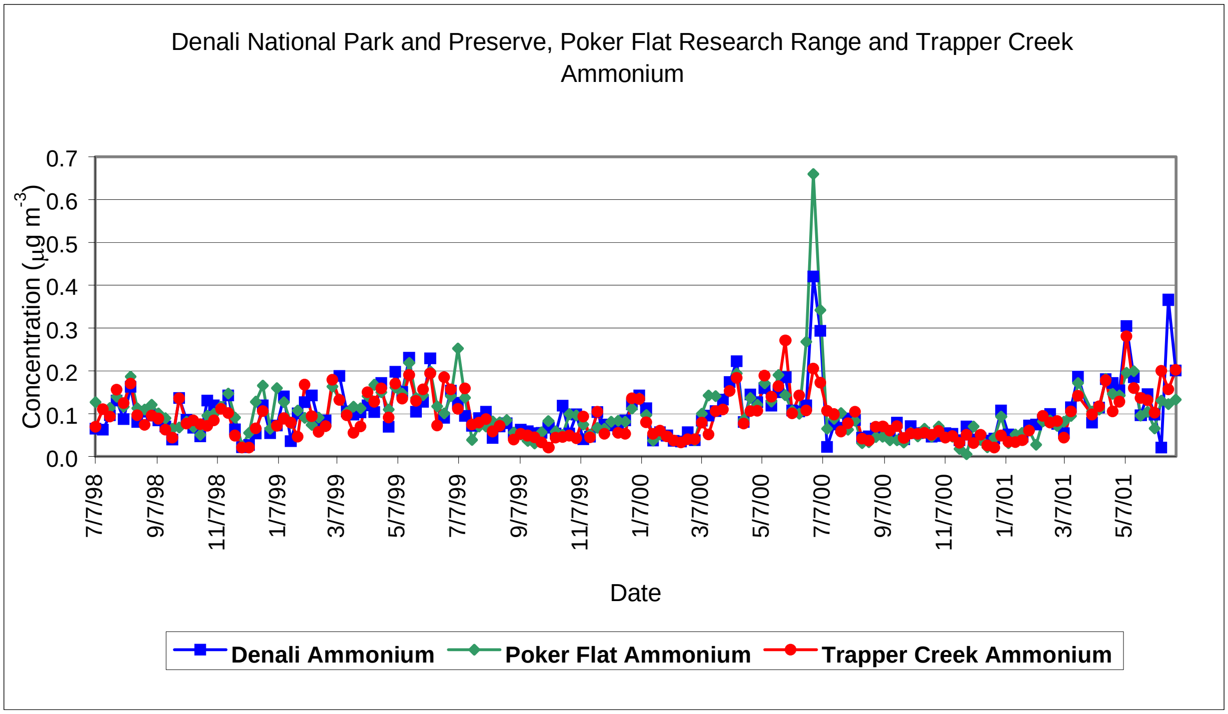


Figure 4-5. Ammonium at Poker Flat, Denali National Park and Preserve, and Trapper Creek, July 1998 to June 2001.

4.1.2 Between Site Correlation for Specific Components

To support the results drawn from the component time-series, a comparison was made for each component between each site and the R^2 values were calculated. The R^2 value is a measure of the relationship between two variables. It is the square of the commonly used correlation coefficient (r). An R^2 value of 1 indicates a perfect correlation between the two variables while an R^2 value of 0 indicates no correlation between the two variables. Figure 4-6 shows an example of a good correlation (R^2 = 0.91) and no correlation (R^2 = 0.00).

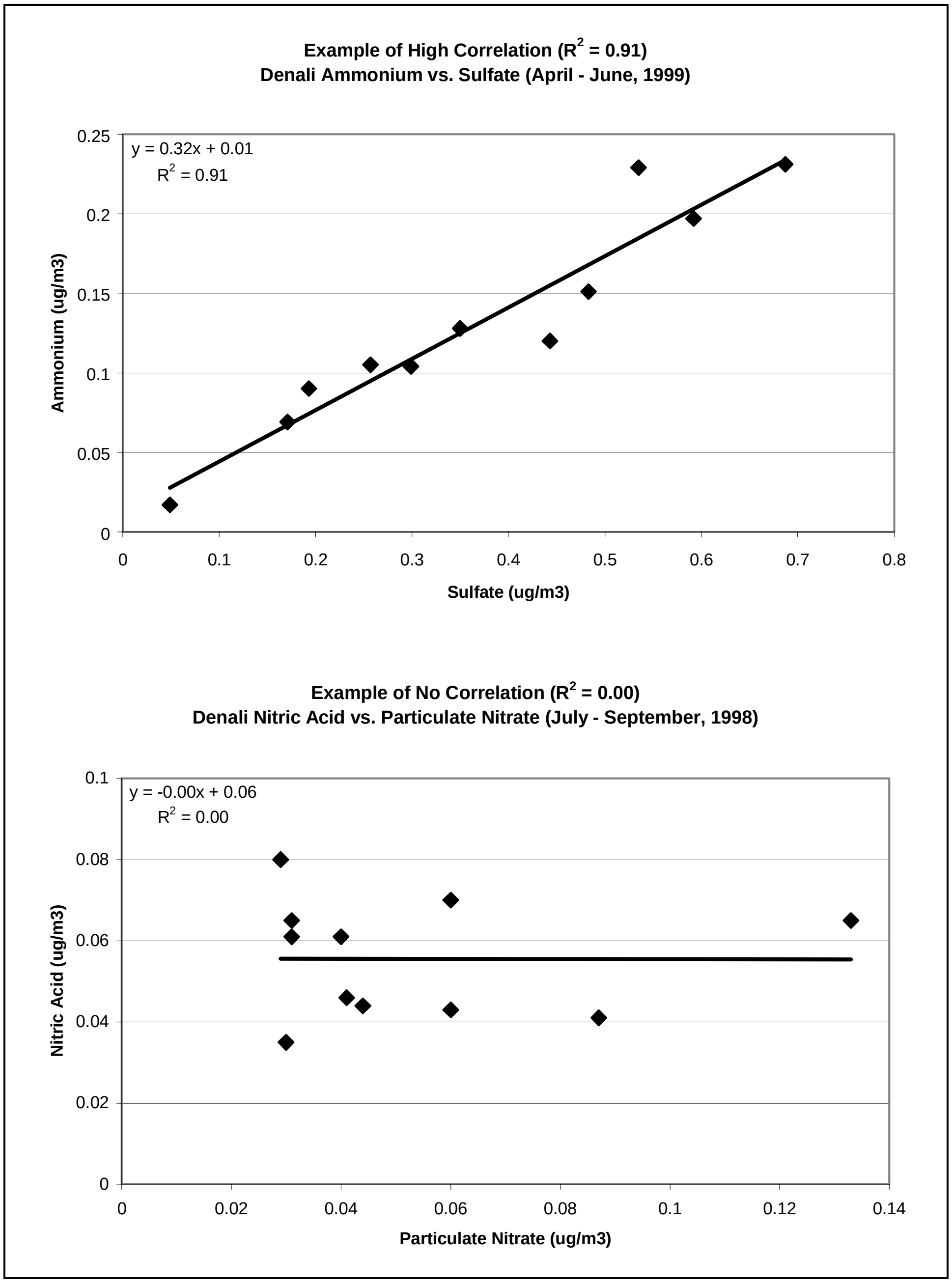


Figure 4-6. Examples of high R^2 values (good correlation) and low R^2 values (no correlation).

Variability in the correlations can be due to a number of factors. If the values are near the minimum detectable limits, the uncertainties in the measurements can dominate the low values and cause a decreased correlation. Also, meteorology can change the correlations between components for each period. For example, if the airflow comes in from a direction that does not have the same emissions sources as the year before, the correlations between the different compounds and sites could be different. Also, for a compound like ammonium nitrate, the temperature and relative humidity can change the amount of the compound in solid form.

Tables that show the R^2 values obtained for the comparisons between components at the three sites for each seasonal and annual period, as well as three-year combined seasonal and annual period may be found in Appendix B. These R^2 values are presented visually in Figures 4-7 through 4-27. The seasons are defined as follows:

Winter	January, February, March
Spring	April, May, June
Summer	July, August, September
Fall	October, November, December

Annual periods are calculated from July through June of the following year. Annual periods are defined as follows:

Year 1	July 1998 – June 1999
Year 2	July 1999 – June 2000
Year 3	July 2000 – June 2001

Sulfate

Figures 4-7 through 4-10 provide graphic views of the R^2 values obtained for the seasonal and yearly comparisons of sulfate at the three sites for each individual year as well as the combined three-year study. In Figure 4-7, the shaded bars represent the seasonal and annual R^2 values for the combined three year period. The error bars represent the highest and lowest between site correlations for an individual year. Tabular R^2 values may be found in Appendix B. The strength of the correlations between the sites varies with year and season:

- Sulfate usually correlates well ($R^2 > 0.50$) between the sites in the summer and winter seasons, the two more regional transport periods. The likely regional sources during these two periods are wildfire smoke (summer) and international transport of pollutants (winter).
- During the fall season, sulfates at Denali and Trapper Creek correlate well in Year 1, but not the other years. The sulfates at Poker Flat do not correlate well with the other two sites during the fall season.
- Sulfates at the three sites do not correlate well during the Year 1 and Year 3 spring seasons. In contrast, during the Year 2 spring season, the sulfate concentrations between Poker Flat and Denali and Denali and Trapper Creek correlate well (0.89 and 0.61, respectively).
- On an annual basis, the sulfates at Poker Flat and Trapper Creek correlated well with Denali. Sulfate correlations between Poker Flat and Trapper Creek did not correlate well, except for Year 3 (R^2=0.63).

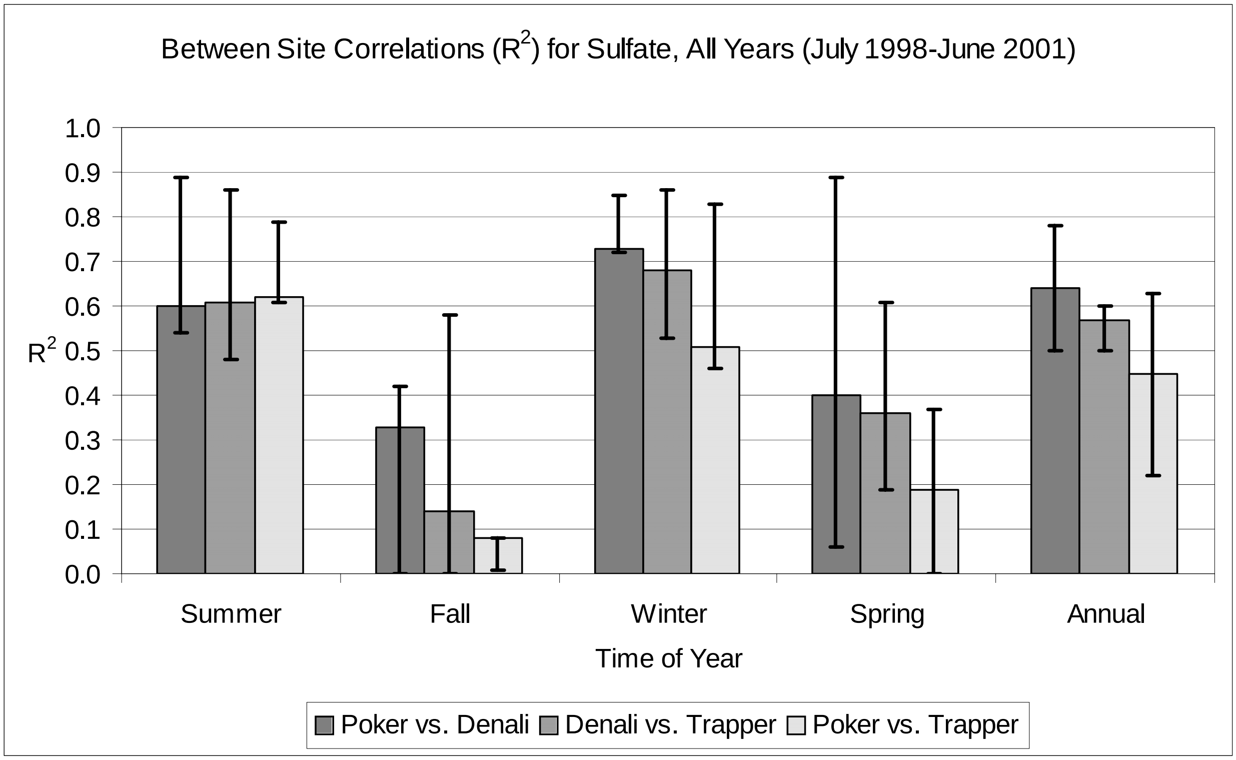


Figure 4-7. Between site correlations for sulfate, All Years (July 1998 through June 2001).

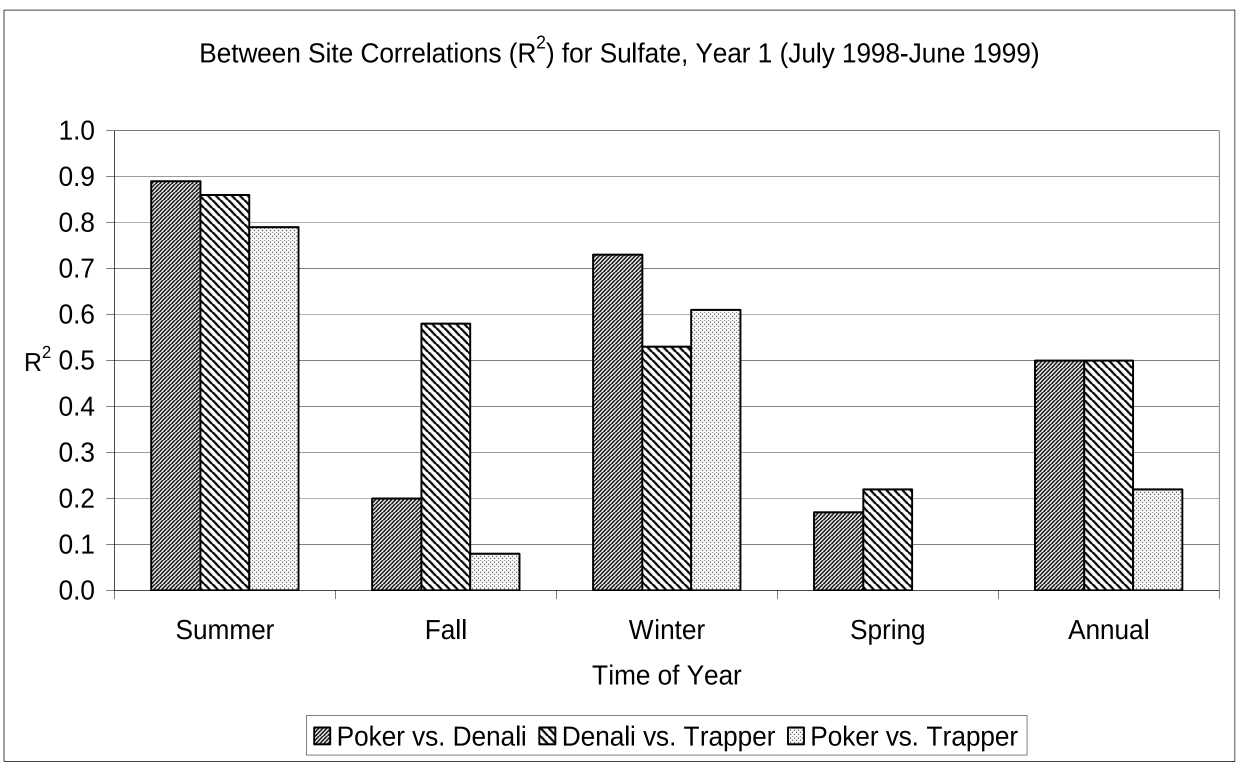


Figure 4-8. Between site correlations for sulfate, Year 1 (July 1998 through June 1999).

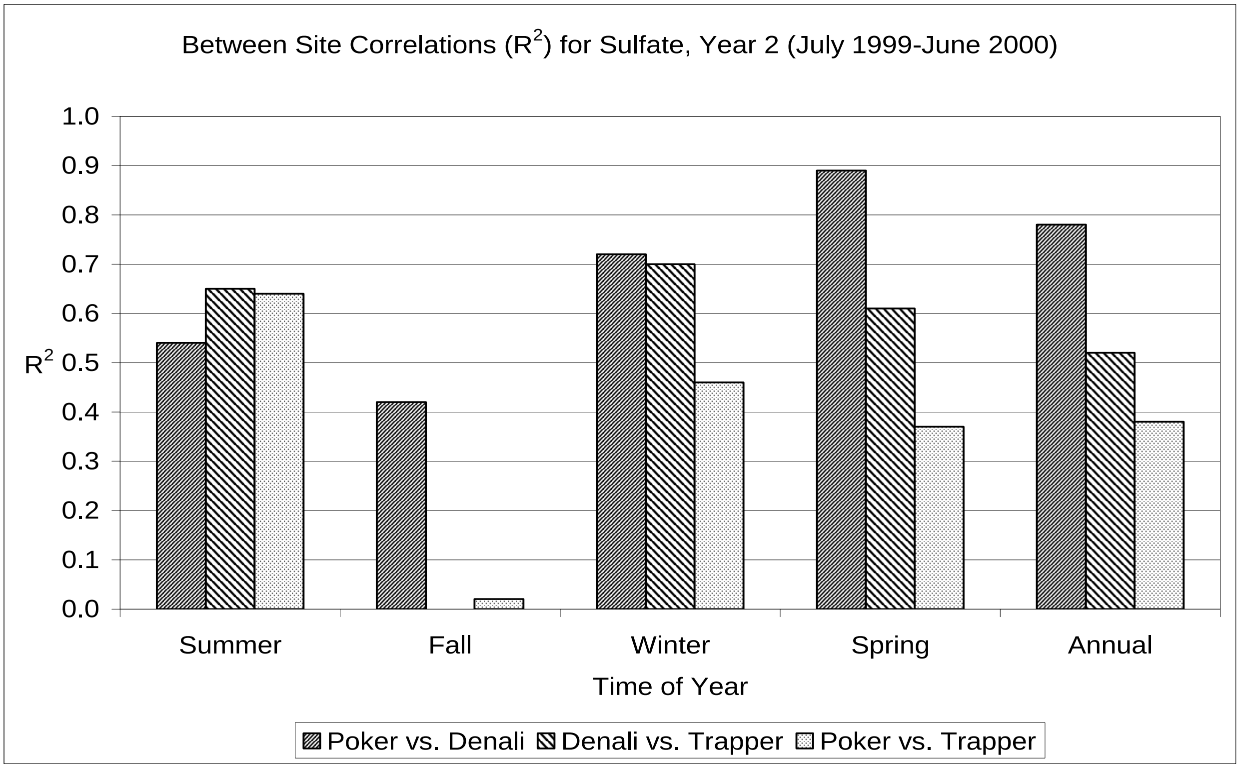


Figure 4-9. Between site correlations for sulfate, Year 2 (July 1999 through June 2000).

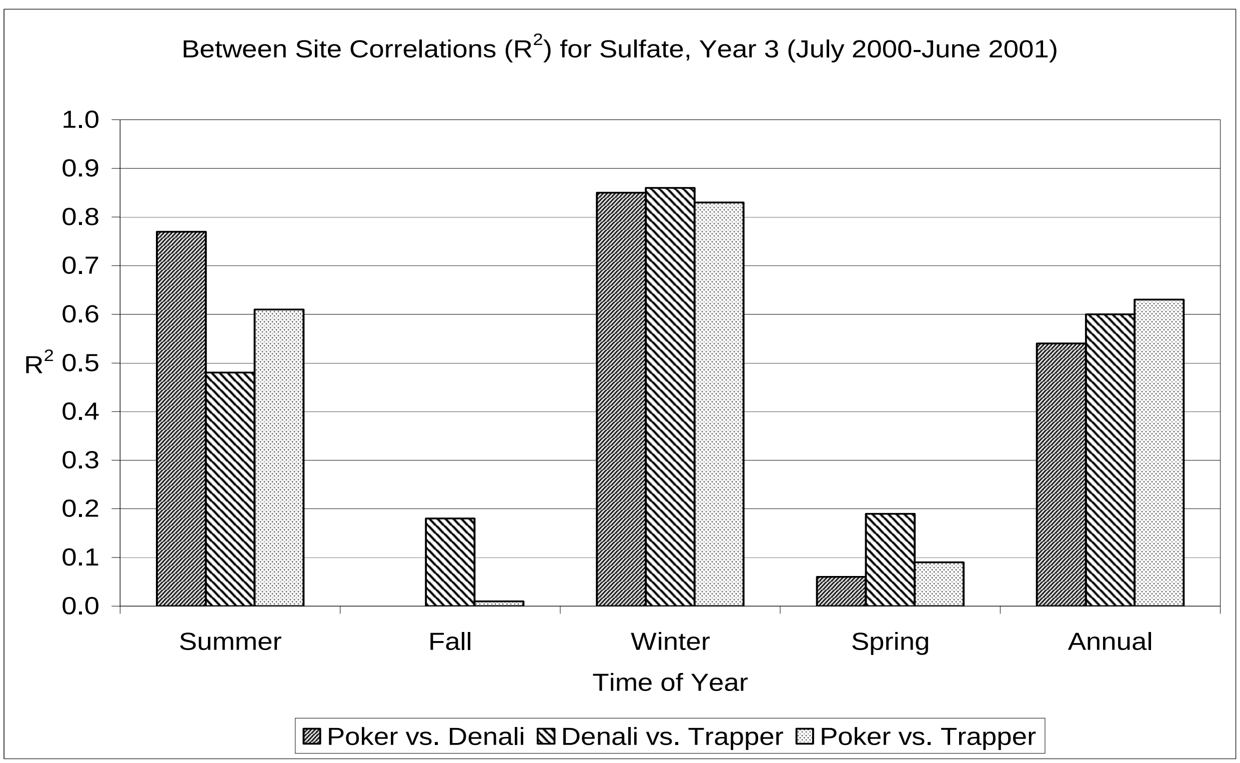


Figure 4-10. Between site correlations for sulfate, Year 3 (July 2000 through June 2001).

Sulfur Dioxide

Figures 4-11 through 4-14 provide graphic views of the R^2 values obtained for the seasonal and yearly comparisons of sulfur dioxide at the three sites for each individual year as well as the combined three-year study. In Figure 4-11, the shaded bars represent the seasonal and annual R^2 values for the combined three year period. The error bars represent the highest and lowest between site correlations for an individual year. Tabular R^2 values may be found in Appendix B. The strength of the correlations between the sites varies:

- Sulfur dioxide correlations between Poker Flat and Trapper Creek were poor for all years and seasons.
- During Year 1, strong correlations were seen for Poker Flat and Denali during the summer, fall and winter seasons, and for Denali and Trapper Creek during the winter season.
- During Year 2, the only good sulfur dioxide correlations occurred between Denali and Trapper Creek during the fall and winter season.
- During Year 3, poor correlations were seen between all of the sites.
- For the three-year combined annual period, the only good correlation occurred during the fall season between Poker Flat and Denali.

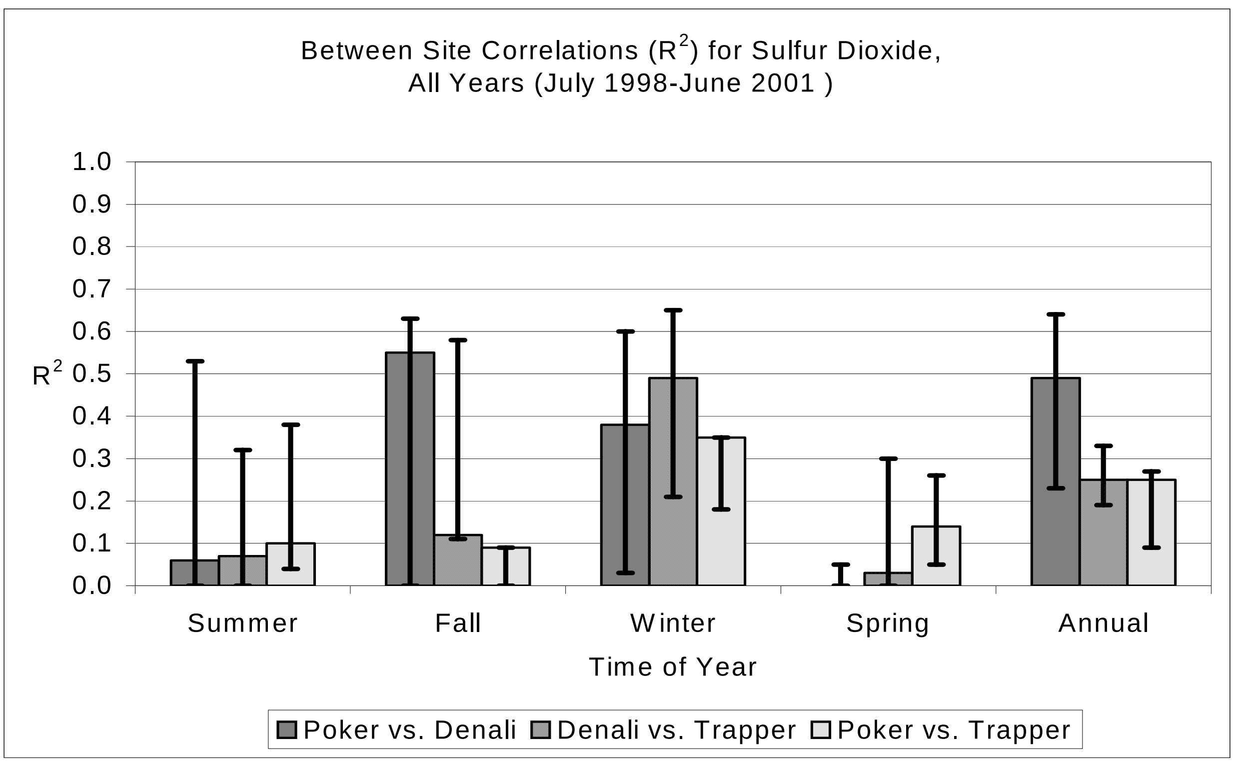


Figure 4-11. Between site correlations for sulfur dioxide, All Years (July 1998 through June 2001).

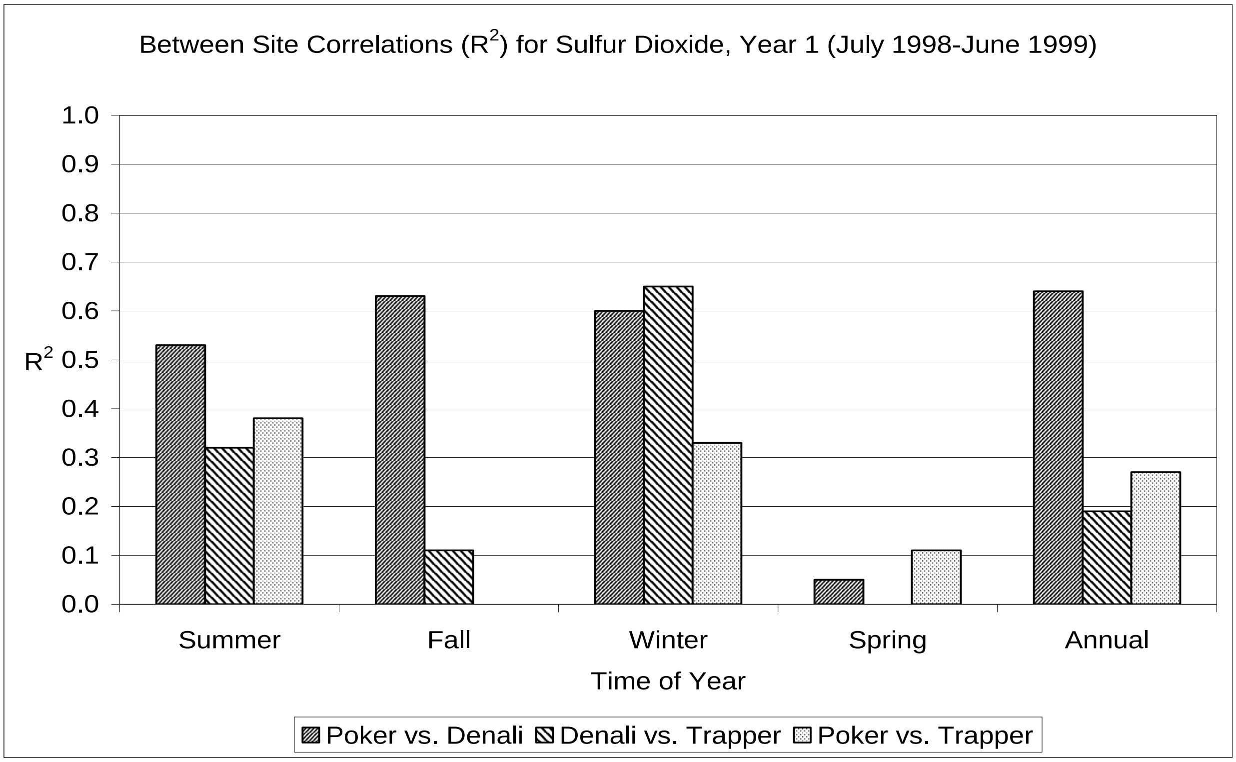


Figure 4-12. Between site correlations for sulfur dioxide, Year 1 (July 1998 through June 1999).

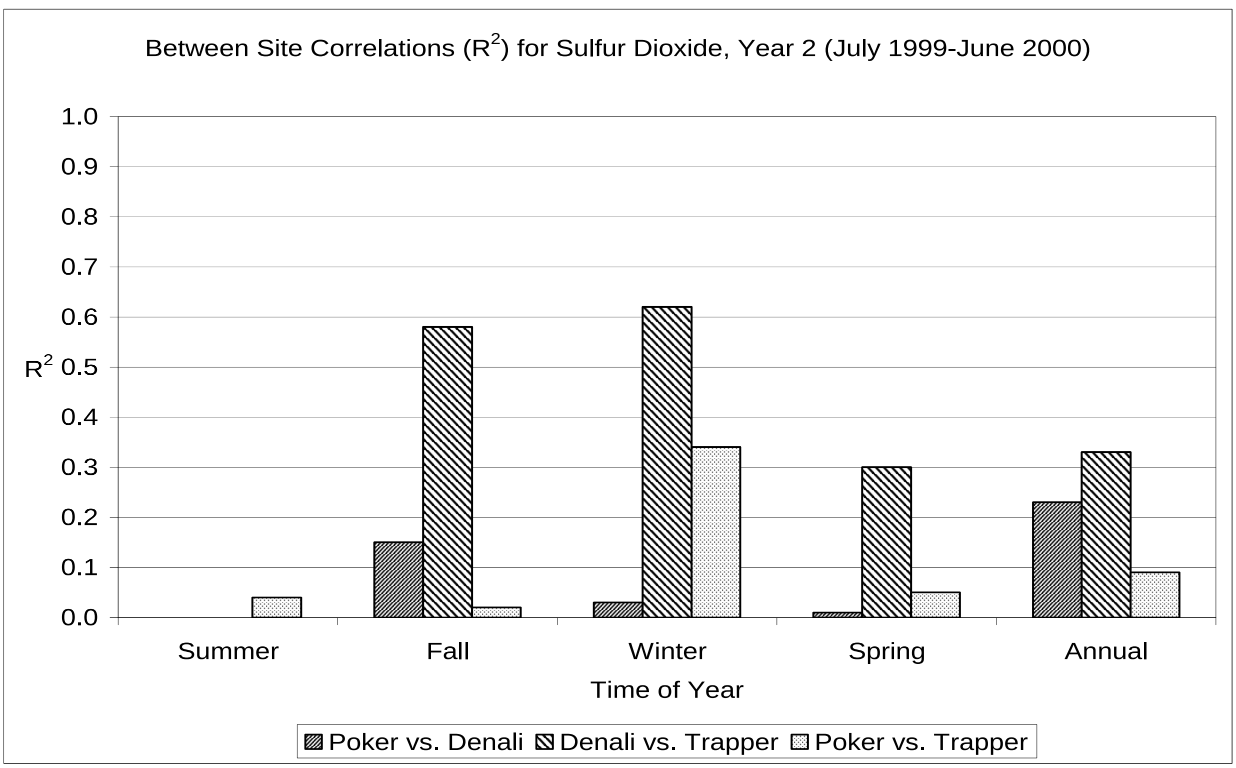


Figure 4-13. Between site correlations for sulfur dioxide, Year 2 (July 1999 through June 2000).

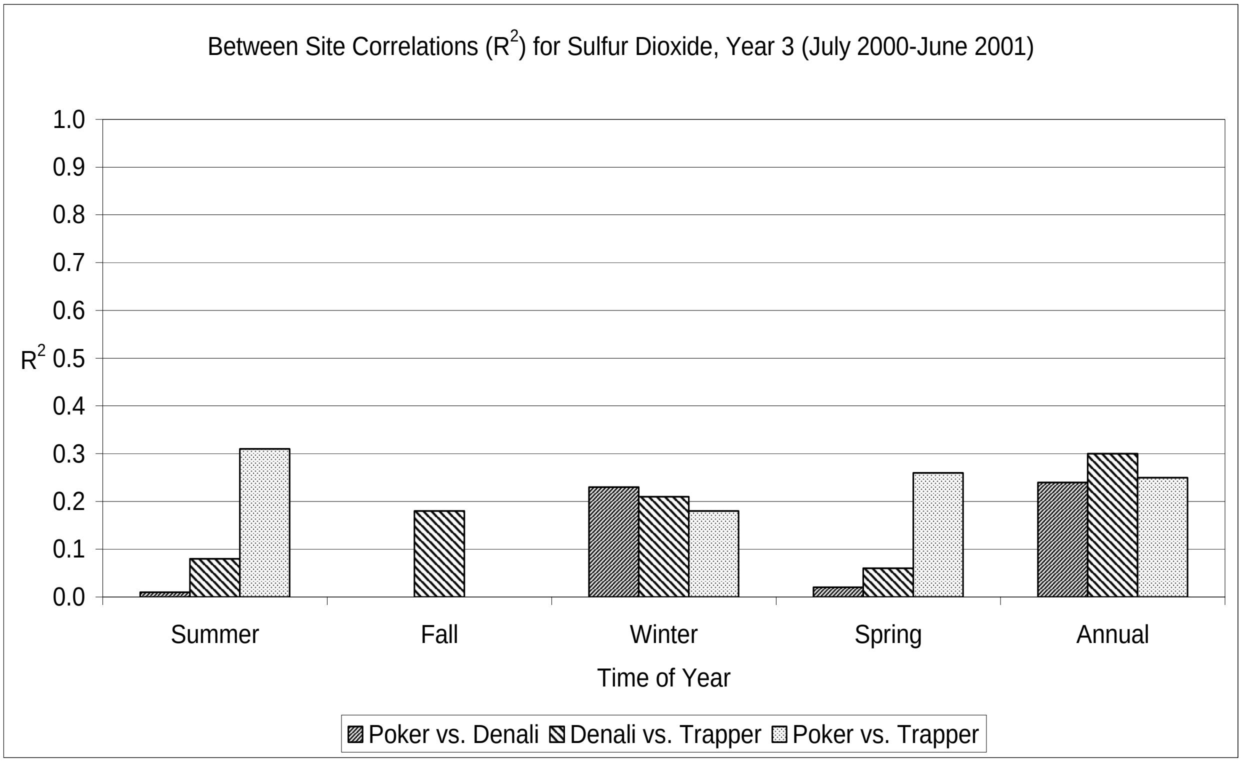


Figure 4-14. Between site correlations for sulfur dioxide, Year 3 (July 2000 through June 2001).

Particulate Nitrate

Figures 4-15 through 4-18 provide graphic views of the R^2 values obtained for the seasonal and yearly comparisons of particulate nitrate at the three sites for each individual year as well as the combined three-year study. In Figure 4-15, the shaded bars represent the seasonal and annual R^2 values for the combined three year period. The error bars represent the highest and lowest between site correlations for an individual year. Tabular R^2 values may be found in Appendix B. Particulate nitrate usually only correlates well between Poker Flat and Denali. The exceptions are:

- The summer season in Year 3 showed good correlations between all three sites.
- The summer season in Year 2 showed good correlations between Poker Flat and Trapper Creek.

The seasons during which the good correlations occurred between Poker Flat and Denali varied dramatically during the three-year study:

- The summer and spring seasons in Year 3 demonstrated good correlation.
- The Year 2 and three-year combined fall season showed good correlation.
- The Year 1, Year 2 and three-year combined winter season demonstrated good correlation.
- On an annual basis, Year 1 demonstrated good correlation.

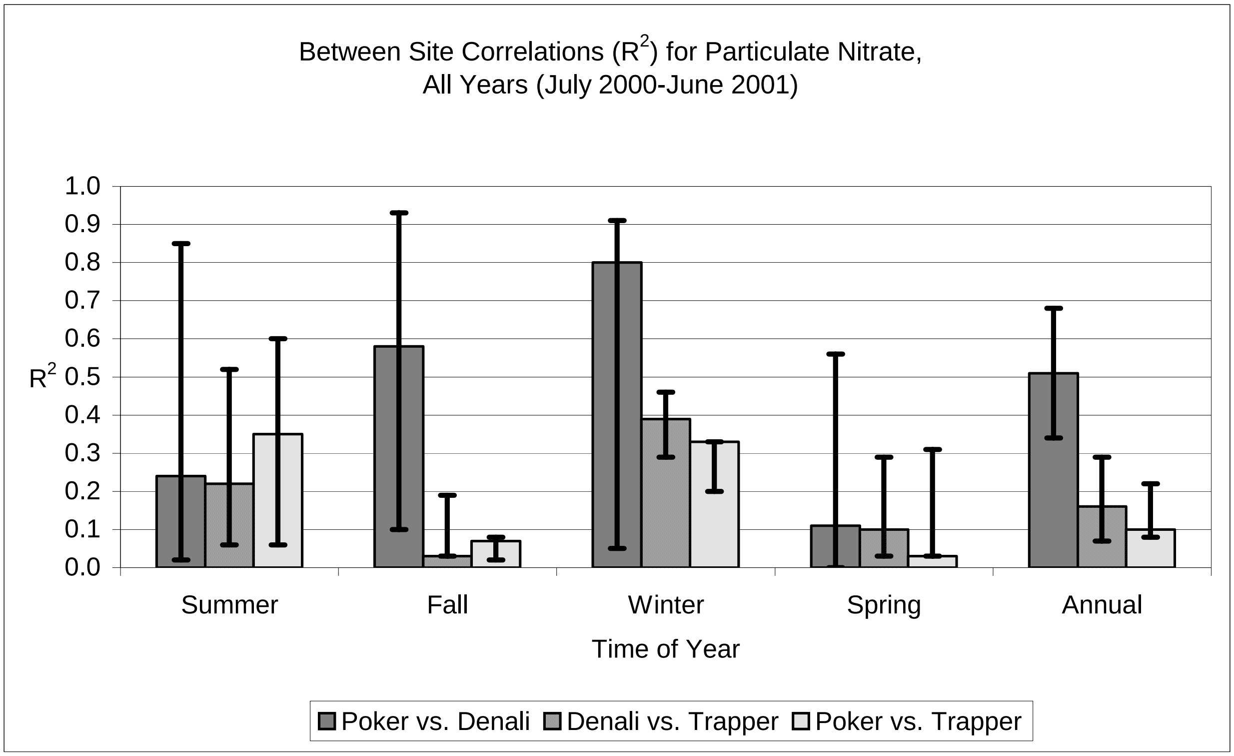


Figure 4-15. Between site correlations for particulate nitrate, All Years (July 1998 through June 2001).

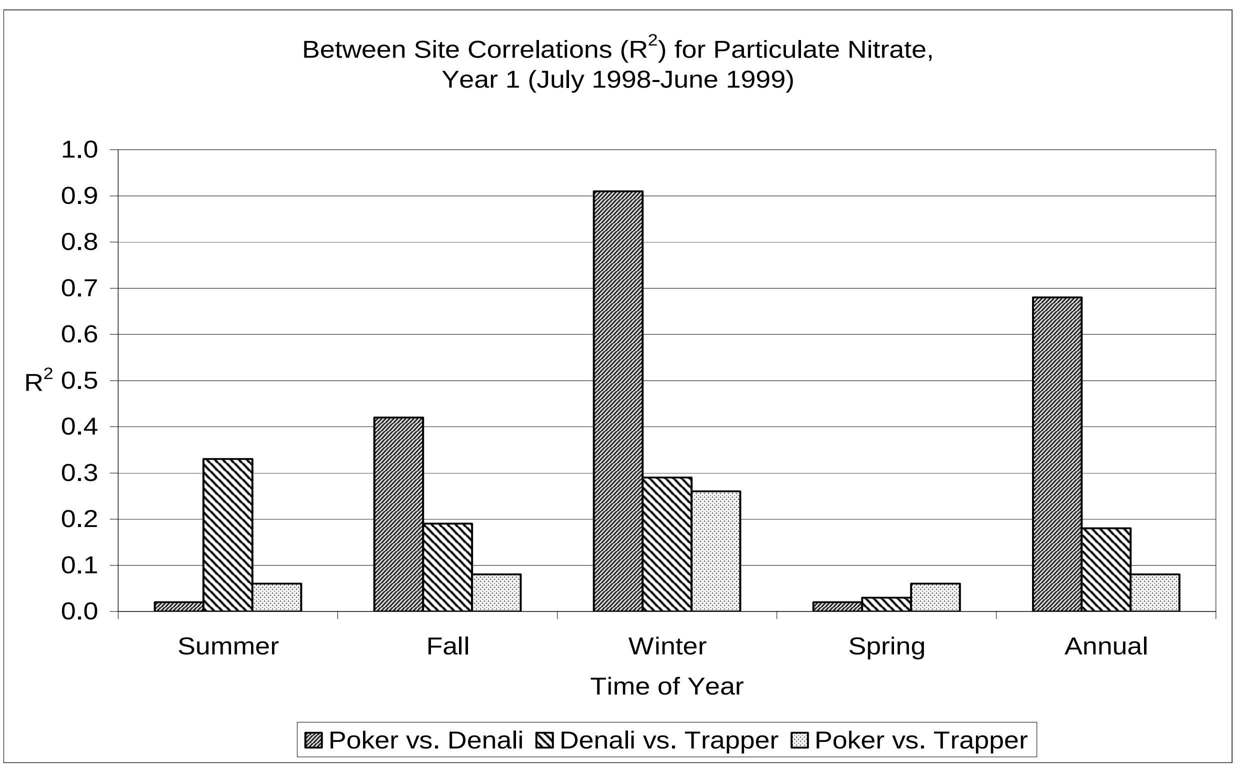


Figure 4-16. Between site correlations for particulate nitrate, Year 1 (July 1998 through June 1999).

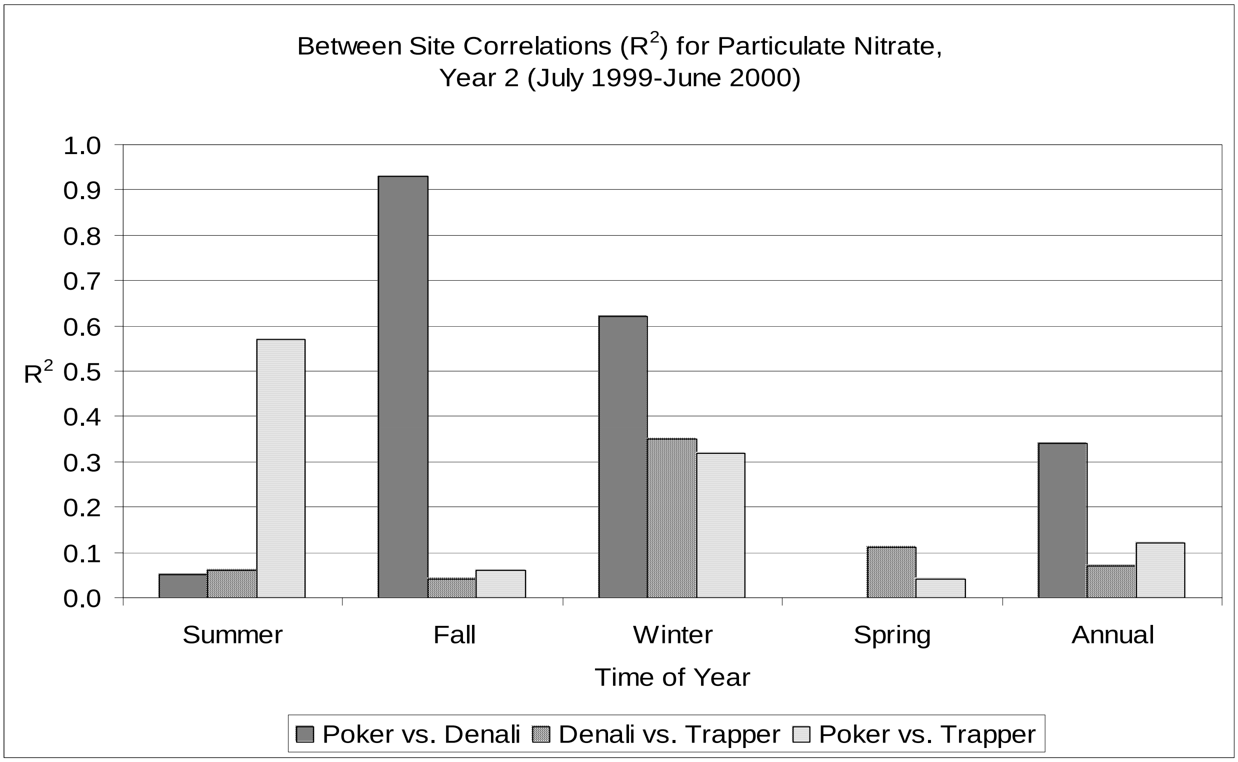


Figure 4-17. Between site correlations for particulate nitrate, Year 2 (July 1999 through June 2000).

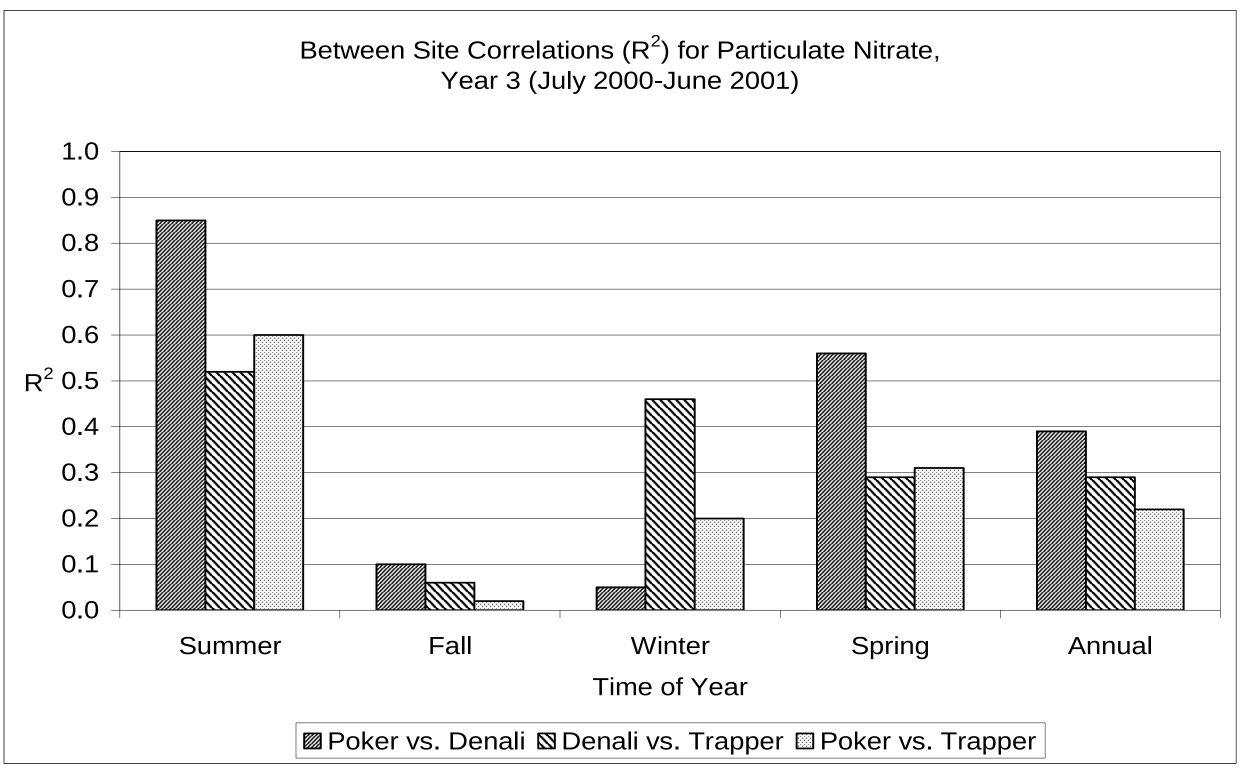


Figure 4-18. Between site correlations for particulate nitrate, Year 3 (July 2000 through June 2001).

Nitric Acid

Figures 4-19 through 4-22 provide graphic views of the R^2 values obtained for the seasonal and yearly comparisons of nitric acid at the three sites for each individual year as well as the combined three-year study. In Figure 4-19, the shaded bars represent the seasonal and annual R^2 values for the combined three year period. The error bars represent the highest and lowest between site correlations for an individual year. Tabular R^2 values may be found in Appendix B. The strength of the correlations between the sites varies seasonally:

- Nitric acid correlates well between sites during the warmer periods, spring and summer seasons.
- Nitric acid does not correlate between the sites during the cold periods, fall and winter seasons. The exception is Year 3 for Denali and Trapper Creek (R^2 = .50).
- On an annual basis, nitric acid correlates well during Year 3 between Denali and Trapper Creek, due to the good correlation seen in the winter season in addition to the typical good correlations in spring and summer.

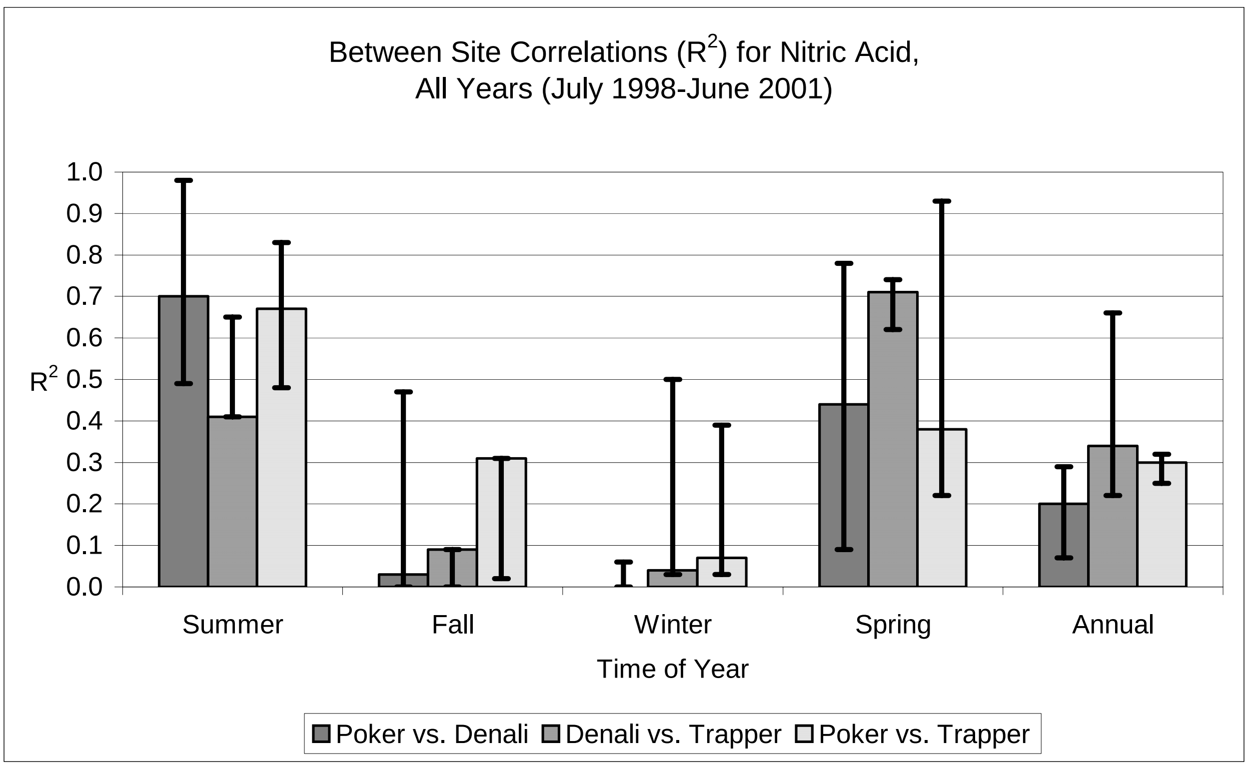


Figure 4-19. Between site correlations for nitric acid, All Years (July 1998 through June 2001).

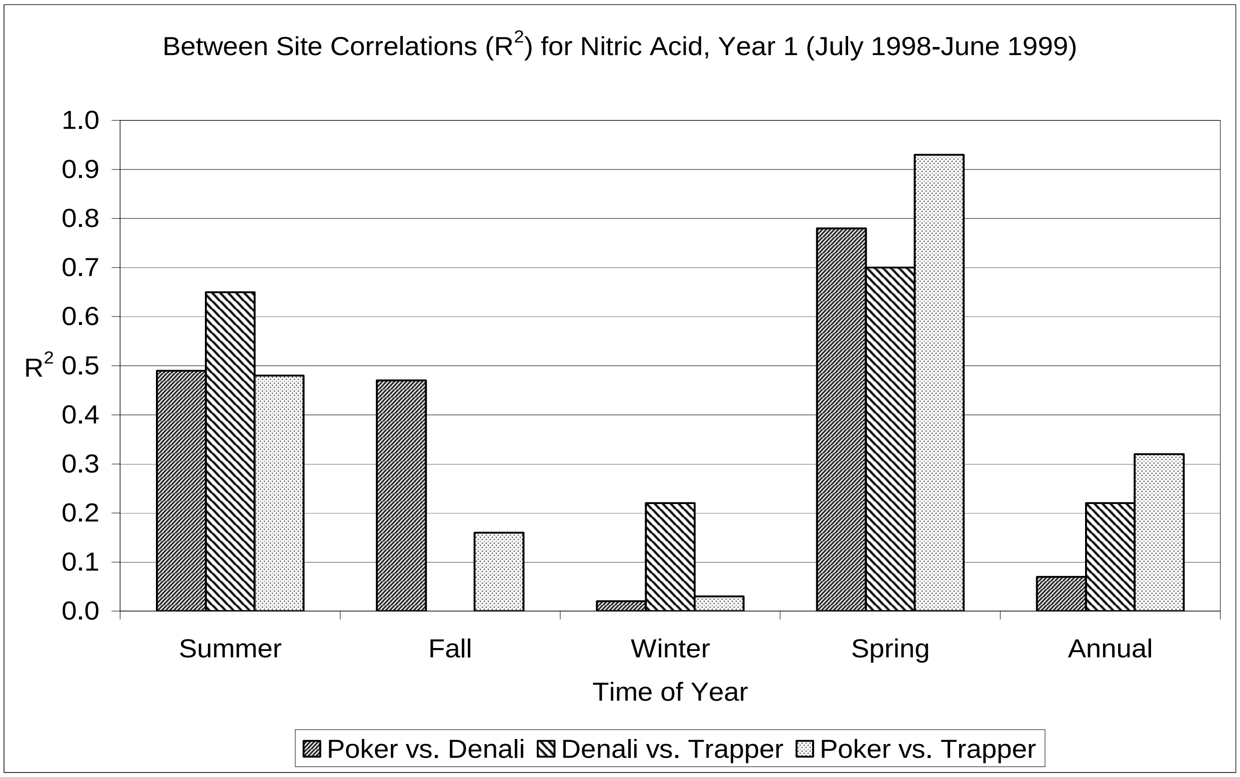


Figure 4-20. Between site correlations for nitric acid, Year 1 (July 1998 through June 1999).

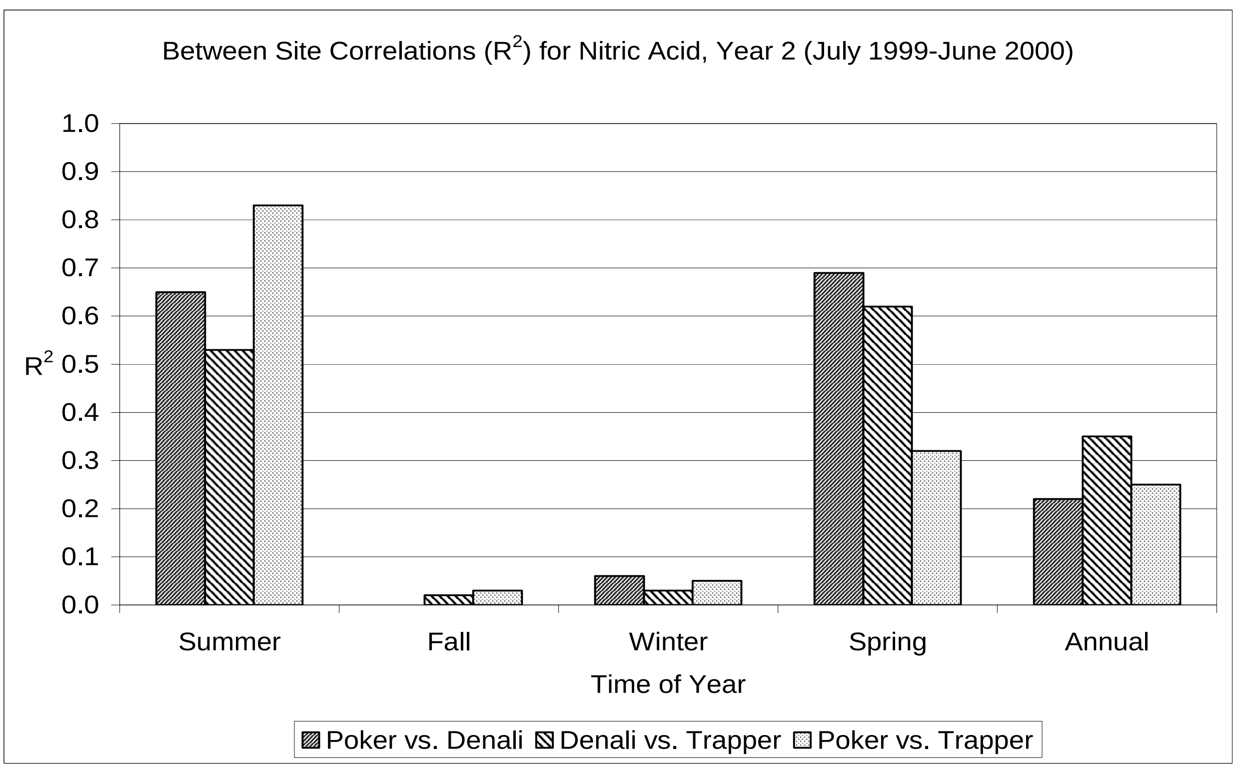


Figure 4-21. Between site correlations for nitric acid, Year 2 (July 1999 through June 2000).

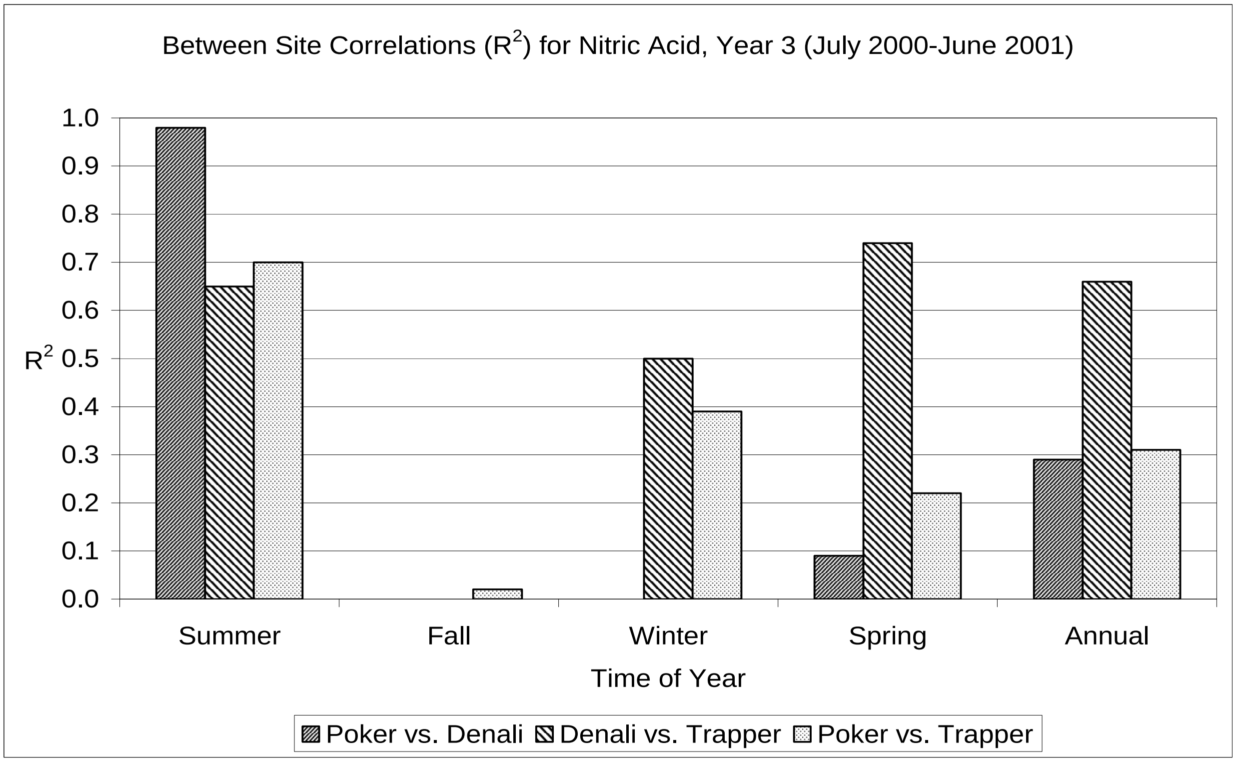


Figure 4-22. Between site correlations for nitric acid, Year 3 (July 2000 through June 2001).

Ammonium

Figures 4-23 through 4-26 provide graphic views of the R^2 values obtained for the seasonal and yearly comparisons of ammonium at the three sites for each individual year as well as the combined three-year study. In Figure 4-23, the shaded bars represent the seasonal and annual R^2 values for the combined three year period. The error bars represent the highest and lowest between site correlations for an individual year. Tabular R^2 values may be found in Appendix B. As with sulfate, the strength of the ammonium correlations between the sites varies with year and season:

- The ammonium correlates well between sites during the summer season, but has large inter-annual variability during the other seasons.
- During the fall season in Year 1, there are good ($R^2 > 0.5$) correlations between ammonium at all three sites.
- Good correlations between Poker Flat and Denali and Denali and Trapper Creek were seen during the Year 2, Year 3, and combined three-year winter seasons.
- Correlations between Poker Flat and Trapper Creek for the winter season are not significant, except Year 3 ($R^2 = 0.70$).
- During the spring season the ammonium correlations between the sites are poor for all cases except Poker Flat and Denali during Year 1 and Year 2.

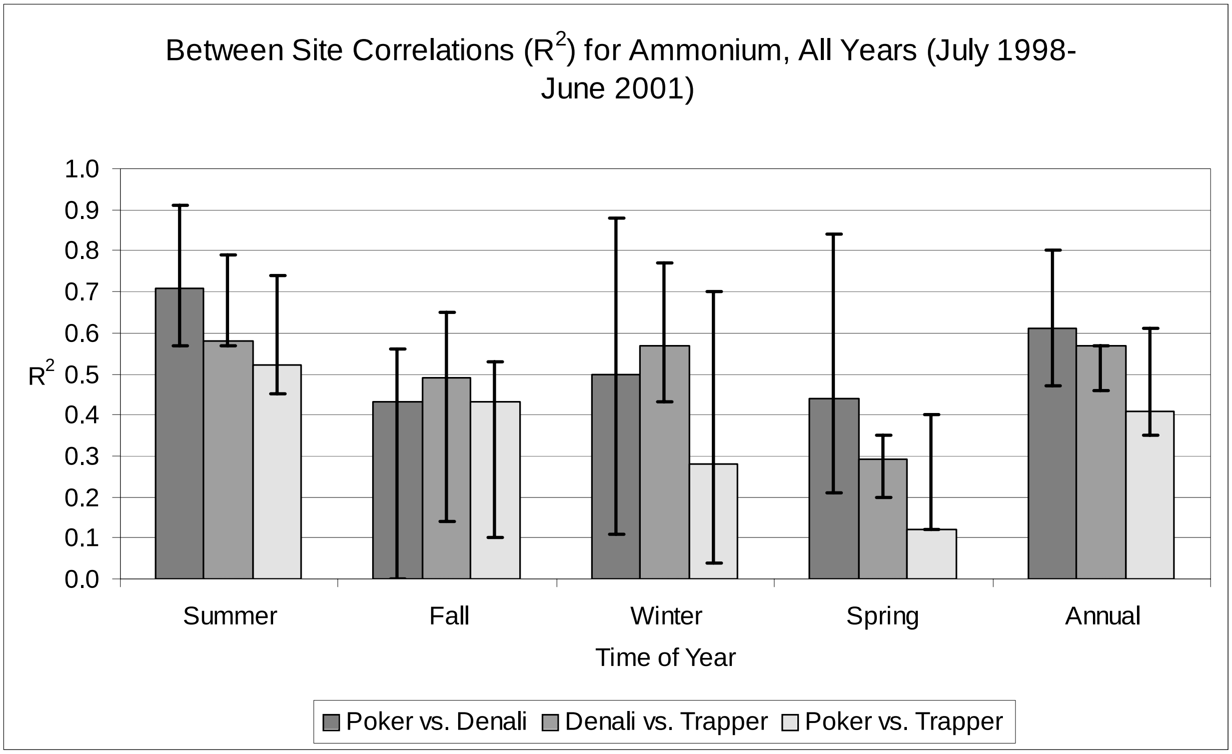


Figure 4-23. Between site correlations for ammonium All Years (July 1998 through June 2001).

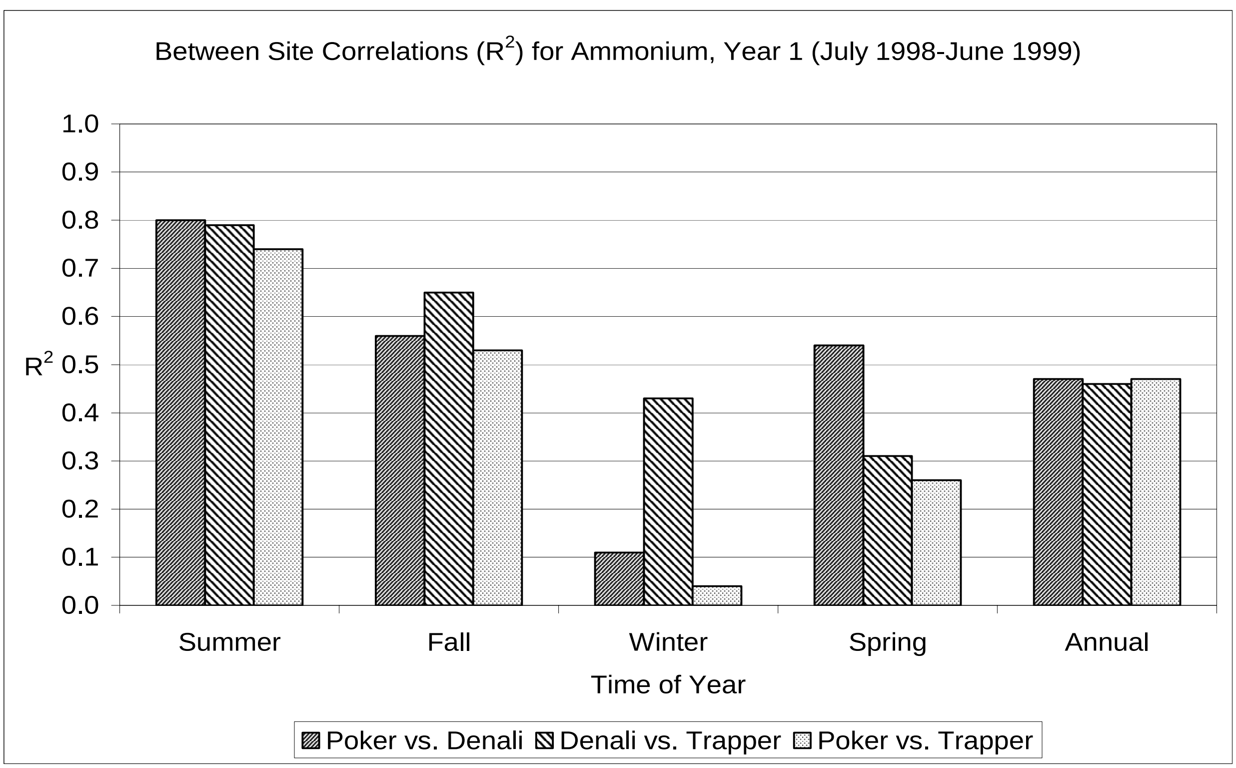


Figure 4-24. Between site correlations for ammonium, Year 1 (July 1998 through June 1999).

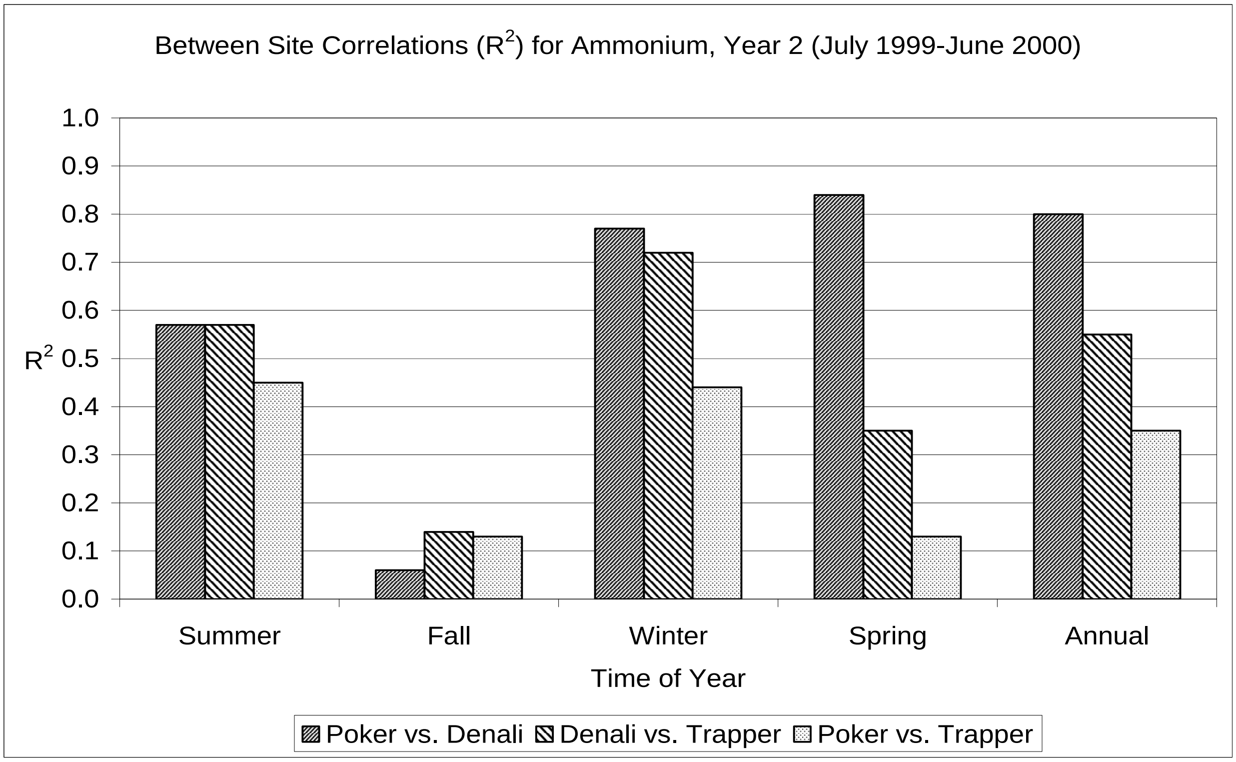


Figure 4-25. Between site correlations for ammonium, Year 2 (July 1999 through June 2000).

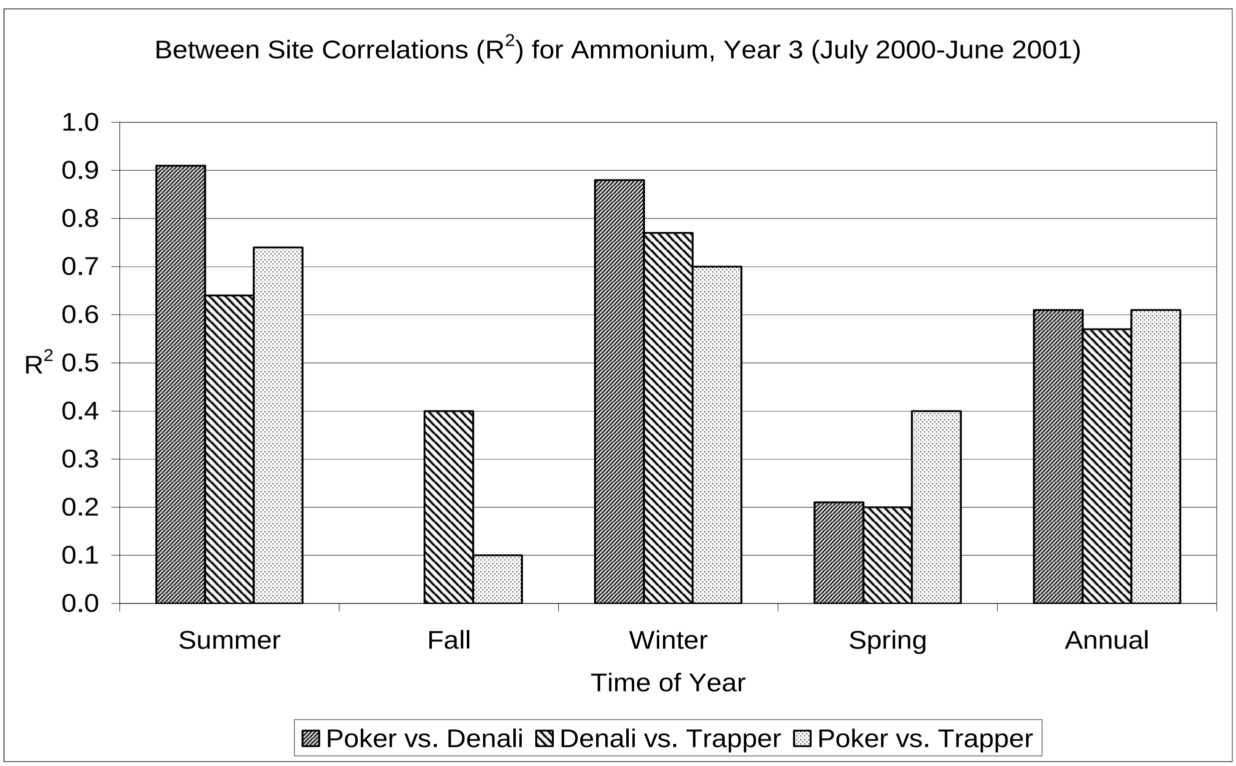


Figure 4-26. Between site correlations for ammonium, Year 3 (July 2000 through June 2001).

4.1.3 Site-specific Between Component Correlations

Tables 4-5 through 4-7 show the between components correlations at each site for each seasonal, annual and three-year combined seasonal and annual periods. In these tables, the R^2 values greater than 0.5 are in bold type while R^2 values less than 0.5 are in normal type. Again, an R^2 of 0.5 corresponds to the division between "good" and "poor" correlations. The correlation between different components at a given site provides information on the potential sources of the observed components.

Sulfate vs. Ammonium

Sulfate and ammonium show good correlations for almost all seasons at all sites. The primary exception is Poker Flat during Year 1, where the summer season showed the only good correlation. Because ammonium sulfate and ammonium bisulfate are the predominant forms of sulfate in the atmosphere, these components should correlate well. The ammonia gas present in the atmosphere reacts with sulfur compounds to form ammonium sulfate and ammonium bisulfate. In the absence of available sulfate or nitrate, ammonia will remain gaseous, and will not convert to ammonium.

Sulfate vs. Sulfur Dioxide

The strength of the correlations between sulfate and sulfur dioxide vary by site:

- At Poker Flat, the components only correlate well during the Year 2 and Year 3 fall seasons.
- At Denali, the components never correlate well.
- At Trapper Creek, the components correlate well for two seasons per year. However, the two seasons vary from year to year.

The poor correlations between the components at Poker Flat and Denali imply that (1) they come from different sources, or (2) if they come from the same source, the source is far enough away that all of the sulfur dioxide has time to convert to sulfate before reaching the site in the daylight periods or remains as sulfur dioxide during the cold, dark periods of winter. Trapper Creek's sulfate/sulfur dioxide correlations, although they are good for two seasons a year, have no distinct seasonal pattern. This implies that the sulfate and sulfur dioxide observed at Trapper Creek are coming from different sources than the sulfate and sulfur dioxide observed at Poker Flat and Denali. This means that meteorology and other sulfur sources are important factors in the Trapper Creek correlation.

Sulfate vs. Particulate Nitrate

The correlations between sulfate and particulate nitrate vary significantly with site and year:

- At Poker Flat, sulfate and particulate nitrate correlate well during one period (Summer, Year 3).

- At Trapper Creek, sulfate and particulate nitrate correlate well during each summer season.
- Denali demonstrates some variability; the components correlate well for most of Year 1 (except for the summer season), do not correlate well during Year 2 and the overall study, and correlate well during the summer season in Year 3.

Sulfate vs. Nitric Acid

Sulfate and nitric acid rarely correlate well at any of the three sites. However, good correlations were seen at Poker Flat and Trapper Creek during the summer seasons in Year 2 and Year 3 and at Denali during the summer and winter seasons in Year 3. This implies a summertime nitric acid source such as wildfire smoke.

Sulfur Dioxide vs. Particulate Nitrate

Denali and Trapper Creek do not show good correlations between sulfur dioxide and particulate nitrate, with the exception of winter and spring of Year 1 at Denali. However, Poker Flat does have some periods of good correlations between the components in the first two years of the study.

Sulfur Dioxide vs. Nitric Acid

The correlations between sulfur dioxide and nitric acid vary significantly with site:

- The correlations between sulfur dioxide and nitric acid are variable at Poker Flat. During Year 1, only the summer period showed a good correlation. The next two years demonstrated good correlations during the fall and winter periods. Year 3 also showed a good correlation during the spring.
- Denali had no good correlations during the study.
- Trapper Creek had a few, spring/summer good correlations.

Again, this indicates different sources of nitric acid and sulfur dioxide reaching the three sites at different times of year.

Ammonium vs. Sulfur Dioxide

All three sites show poor correlations between ammonium and sulfur dioxide. This is to be expected since sulfur dioxide and ammonium originate from different sources and the ammonia gas present in the atmosphere does not react with sulfur dioxide as it does with sulfate.

Ammonium vs. Particulate Nitrate

All three sites show poor correlations between ammonium and particulate nitrate with occasional good correlations between the components during spring/summer periods at Poker Flat and Trapper Creek.

Ammonium vs. Nitric Acid

All three sites show good correlations between ammonium and nitric acid during the summer in Years 2 and 3. Good correlations are also seen in the spring at Poker Flat (Year 2) and Denali (all years) as well as in the winter of Year 3 at Denali.

Particulate Nitrate vs. Nitric Acid

The particulate nitrate and nitric acid correlations are poor for almost every season at all three sites. The cause of this is difficult to determine because, as explained in the Background section, this could be due to particulate nitrate and nitric acid coming from different sources, changes in the relative humidity leading to a predominance of one form or the other, temperature increases causing the ammonium nitrate to volatize, or the abundance of ammonium.

4.1.4 National Standards

In the context of air quality across the United States, these sites are very clean.

- According to the Interagency Monitoring of Protected Visual Environments (IMPROVE) network, the annual average concentration of fine mass at Denali National Park and Preserve was 1.4µg m^{-3} between 1996 and 1998 (http://vista.cira.colostate.edu/improve/Data/GraphicViewer/seasonal.htm). It is the lowest annual average fine mass concentration in the IMPROVE network during this period. However, despite Denali's clean air, the chemical components reaching Denali show that Denali is experiencing the effects of international transport, such as sulfur compounds brought in during Arctic Haze episodes.
- The National Ambient Air Quality Standard (NAAQS) for annual average fine mass is 15µg m^{-3} so Denali's weekly fine mass is less than one tenth of the annual NAAQS for fine mass.
- The NAAQS for sulfur dioxide is an annual arithmetic mean of 0.03 ppm or ~ 80µg m^{-3} (http://www.epa.gov/airs/criteria.html) so Denali's highest, weekly-averaged, sulfur dioxide concentration of 3.10µg m^{-3} is far below the annual NAAQS for sulfur dioxide.

Table 4-1

R^2 for between component comparisons at Poker Flat, All Years (July 1998 – June 2001).

Poker Flat	Summer	Fall	Winter	Spring	Annual
Year 1 (July 1998 – June 1999)					
SO_4 vs. NH_4	**0.55**	0.49	0.12	0.42	0.40
SO_4 vs. SO_2	0.26	0.16	0.22	0.05	0.07
SO_4 vs. pNO_3	0.08	0.02	0.17	0.15	0.07
SO_4 vs. HNO_3	0.04	0.04	0.03	0.11	0.01
SO_2 vs. pNO_3	0.00	**0.72**	**0.73**	0.16	**0.71**
SO_2 vs. HNO_3	**0.71**	0.09	0.03	0.13	0.07
NH_4 vs. SO_2	**0.50**	0.03	0.04	0.00	0.06
NH_4 vs. pNO_3	0.27	0.19	0.10	0.03	0.07
NH_4 vs. HNO_3	0.32	0.00	0.01	0.09	0.02
pNO_3 vs. HNO_3	0.00	0.03	0.05	0.06	0.00
Year 2 (July 1999 – June 2000)					
SO_4 vs. NH_4	**0.90**	**0.71**	**0.74**	**0.52**	**0.51**
SO_4 vs. SO_2	0.03	**0.52**	0.22	0.09	0.07
SO_4 vs. pNO_3	0.27	0.07	0.10	0.36	0.23
SO_4 vs. HNO_3	**0.87**	0.18	0.38	0.20	0.21
SO_2 vs. pNO_3	0.06	0.17	**0.67**	**0.59**	0.26
SO_2 vs. HNO_3	0.02	**0.72**	**0.53**	**0.62**	0.25
NH_4 vs. SO_2	0.01	**0.52**	0.00	0.36	0.00
NH_4 vs. pNO_3	0.34	0.15	0.00	**0.90**	0.32
NH_4 vs. HNO_3	**0.86**	0.33	0.07	**0.80**	0.35
pNO_3 vs. HNO_3	0.23	0.27	0.09	**0.91**	0.33
Year 3 (July 2000 – June 2001)					
SO_4 vs. NH_4	**0.94**	0.42	**0.81**	**0.59**	**0.59**
SO_4 vs. SO_2	0.17	**0.57**	0.28	0.05	0.10
SO_4 vs. pNO_3	**0.85**	0.42	0.00	0.37	0.29
SO_4 vs. HNO_3	**0.94**	0.44	0.07	0.04	0.13
SO_2 vs. pNO_3	0.09	0.45	0.02	0.03	0.11
SO_2 vs. HNO_3	0.25	**0.56**	**0.53**	0.13	0.18
NH_4 vs. SO_2	0.16	0.30	0.09	0.02	0.01
NH_4 vs. pNO_3	**0.86**	0.07	0.04	0.21	0.19
NH_4 vs. HNO_3	**0.96**	0.48	0.02	0.00	0.36
pNO_3 vs. HNO_3	**0.87**	0.16	0.01	0.13	0.03
All Years (July 1998 – June 2001)					
SO_4 vs. NH_4	**0.78**	0.37	**0.56**	0.42	0.49
SO_4 vs. SO_2	0.07	0.40	0.09	0.00	0.06
SO_4 vs. pNO_3	0.34	0.07	0.04	0.35	0.14
SO_4 vs. HNO_3	**0.62**	0.15	0.15	0.01	0.08
SO_2 vs. pNO_3	0.03	0.47	**0.69**	0.15	0.49
SO_2 vs. HNO_3	0.12	0.32	0.09	0.32	0.13
NH_4 vs. SO_2	0.02	0.09	0.02	0.13	0.00
NH_4 vs. pNO_3	0.46	0.01	0.00	**0.64**	0.09
NH_4 vs. HNO_3	**0.68**	0.23	0.03	0.37	0.20
pNO_3 vs. HNO_3	0.35	0.17	0.00	0.19	0.06

Table 4-2

R^2 for between component comparisons at Denali, All Years (July 1998 – June 2001).

Denali	Summer	Fall	Winter	Spring	Annual
Year 1 (July 1998 – June 1999)					
SO_4 vs. NH_4	**0.76**	**0.74**	0.26	**0.91**	**0.69**
SO_4 vs. SO_2	0.40	0.08	0.41	0.30	0.01
SO_4 vs. pNO_3	0.35	**0.71**	**0.50**	**0.55**	0.23
SO_4 vs. HNO_3	0.32	0.03	0.00	0.28	0.07
SO_2 vs. pNO_3	0.07	0.32	**0.70**	**0.80**	0.39
SO_2 vs. HNO_3	0.16	0.03	0.02	0.02	0.00
NH_4 vs. SO_2	0.22	0.15	0.09	0.19	0.01
NH_4 vs. pNO_3	0.10	0.49	0.01	0.39	0.01
NH_4 vs. HNO_3	0.24	0.13	0.15	**0.53**	0.22
pNO_3 vs. HNO_3	0.00	0.02	0.14	0.05	0.02
Year 2 (July 1999 – June 2000)					
SO_4 vs. NH_4	**0.78**	**0.64**	**0.81**	**0.68**	**0.72**
SO_4 vs. SO_2	0.10	0.43	0.39	0.37	0.05
SO_4 vs. pNO_3	0.00	0.13	0.22	0.09	0.06
SO_4 vs. HNO_3	0.40	0.02	0.15	0.27	0.22
SO_2 vs. pNO_3	0.00	0.27	0.42	0.07	0.27
SO_2 vs. HNO_3	0.05	0.20	0.41	0.03	0.02
NH_4 vs. SO_2	0.16	0.15	0.48	0.18	0.00
NH_4 vs. pNO_3	0.05	0.00	0.10	0.03	0.00
NH_4 vs. HNO_3	**0.60**	0.09	0.38	**0.72**	**0.54**
pNO_3 vs. HNO_3	0.10	0.02	0.00	0.02	0.00
Year 3 (July 2000 – June 2001)					
SO_4 vs. NH_4	**0.93**	0.12	**0.81**	**0.92**	**0.83**
SO_4 vs. SO_2	0.23	0.39	0.34	0.46	0.15
SO_4 vs. pNO_3	**0.62**	0.16	0.40	0.48	0.41
SO_4 vs. HNO_3	**0.81**	0.00	**0.60**	0.49	**0.51**
SO_2 vs. pNO_3	0.13	0.29	0.05	0.09	0.00
SO_2 vs. HNO_3	0.08	0.09	0.38	0.41	0.03
NH_4 vs. SO_2	0.12	0.01	0.32	0.44	0.03
NH_4 vs. pNO_3	**0.75**	0.21	0.36	0.28	0.45
NH_4 vs. HNO_3	**0.95**	0.01	**0.82**	**0.69**	**0.76**
pNO_3 vs. HNO_3	**0.81**	0.00	0.21	0.02	0.27
All Years (July 1998 – June 2001)					
SO_4 vs. NH_4	**0.80**	**0.52**	**0.60**	**0.80**	**0.74**
SO_4 vs. SO_2	0.07	0.05	0.34	0.36	0.03
SO_4 vs. pNO_3	0.36	0.03	0.23	0.15	0.18
SO_4 vs. HNO_3	0.42	0.14	0.19	0.23	0.22
SO_2 vs. pNO_3	0.01	0.24	0.47	0.14	0.23
SO_2 vs. HNO_3	0.08	0.17	0.08	0.06	0.01
NH_4 vs. SO_2	0.03	0.00	0.32	0.24	0.00
NH_4 vs. pNO_3	0.44	0.00	0.09	0.08	0.07
NH_4 vs. HNO_3	**0.58**	0.27	0.37	**0.54**	0.48
pNO_3 vs. HNO_3	0.18	0.02	0.01	0.00	0.01

Table 4-3

R^2 for between component comparisons at Trapper Creek, All Years (July 1998 through June 2001).

Trapper Creek	Summer	Fall	Winter	Spring	Annual
Year 1 (July 1998 – June 2001)					
SO_4 vs. NH_4	**0.83**	**0.73**	0.44	**0.73**	**0.68**
SO_4 vs. SO_2	**0.65**	0.22	0.29	**0.52**	0.08
SO_4 vs. pNO_3	**0.55**	0.01	0.06	0.30	0.20
SO_4 vs. HNO_3	0.44	0.16	0.02	**0.63**	0.00
SO_2 vs. pNO_3	0.21	0.04	0.00	0.38	0.03
SO_2 vs. HNO_3	0.41	0.01	0.07	**0.79**	0.04
NH_4 vs. SO_2	0.43	0.02	**0.50**	0.41	0.04
NH_4 vs. pNO_3	**0.55**	0.00	0.03	**0.53**	0.11
NH_4 vs. HNO_3	0.40	0.12	0.08	0.38	0.01
pNO_3 vs. HNO_3	0.31	0.16	0.12	0.22	0.01
Year 2 (July 1999 – June 2000)					
SO_4 vs. NH_4	**0.95**	0.16	**0.71**	**0.93**	**0.78**
SO_4 vs. SO_2	0.30	0.00	**0.50**	**0.67**	0.04
SO_4 vs. pNO_3	**0.54**	0.14	0.08	0.18	0.25
SO_4 vs. HNO_3	**0.68**	0.02	0.01	0.11	0.25
SO_2 vs. pNO_3	0.02	0.05	0.15	0.27	0.01
SO_2 vs. HNO_3	0.20	0.26	0.02	0.23	0.01
NH_4 vs. SO_2	0.38	0.36	0.39	**0.66**	0.04
NH_4 vs. pNO_3	0.38	0.00	0.05	0.34	0.26
NH_4 vs. HNO_3	**0.58**	0.31	0.00	0.21	0.33
pNO_3 vs. HNO_3	**0.55**	0.21	0.09	**0.62**	0.26
Year 3 (July 2000 – June 2001)					
SO_4 vs. NH_4	**0.86**	0.09	**0.95**	**0.80**	**0.85**
SO_4 vs. SO_2	0.37	**0.51**	**0.66**	0.08	0.30
SO_4 vs. pNO_3	**0.75**	0.22	0.04	0.37	**0.53**
SO_4 vs. HNO_3	**0.67**	0.03	0.32	0.15	0.36
SO_2 vs. pNO_3	0.28	0.01	0.01	0.25	0.09
SO_2 vs. HNO_3	**0.67**	0.00	0.17	**0.53**	0.11
NH_4 vs. SO_2	0.40	0.04	**0.57**	0.02	0.12
NH_4 vs. pNO_3	**0.56**	0.02	0.05	0.11	0.49
NH_4 vs. HNO_3	**0.81**	0.14	0.43	0.15	**0.51**
pNO_3 vs. HNO_3	0.45	0.11	0.02	0.12	0.38
All Years (July 1998 – June 2001)					
SO_4 vs. NH_4	0.00	0.24	**0.64**	**0.81**	0.11
SO_4 vs. SO_2	0.10	0.06	0.34	0.22	0.09
SO_4 vs. pNO_3	**0.58**	0.00	0.05	0.27	0.32
SO_4 vs. HNO_3	**0.54**	0.01	0.00	0.17	0.08
SO_2 vs. pNO_3	0.00	0.03	0.05	0.24	0.04
SO_2 vs. HNO_3	0.12	0.11	0.05	**0.56**	0.06
NH_4 vs. SO_2	0.16	0.26	0.47	0.20	0.04
NH_4 vs. pNO_3	0.01	0.01	0.02	0.24	0.04
NH_4 vs. HNO_3	0.00	0.17	0.03	0.19	0.01
pNO_3 vs. HNO_3	0.37	0.22	0.03	0.28	0.13

4.2 METEOROLOGICAL DATA

Wind direction and wind speed results are presented in Appendix C as quarterly and annual wind roses. Temperature data are not addressed in this report.

4.2.1 Poker Flat Air Flow

Air flow in the Poker Flat area is very seasonal and typical of the Alaska interior. The region experiences cold, dry northerly air flow in the winter months and southerly air flow from the Gulf of Alaska in the summer. Winds were monitored from July 1, 1998 to June 30, 2001. During the July to August periods the winds were primarily out of the west-southwest to southwest. During the month of September the winds transitioned from west-southwest to east-northeast. During the Fall/Winter seasons (October to March) the winds were primarily out of the east-northeast. April was a month of transitioning from east-northeast back to west-southwest. The winds from May to June were back to the summer air flow pattern of west-southwest to southwest. The Poker Flat station is in the Chatanika River drainage and the winds are heavily influenced by the orientation of the valley, west-southwest to east-northeast (Appendix C).

4.2.2 Denali National Park and Preserve Air Flow

Air flow in the Denali National Park site is complex. Complex topographic features of the local area affect northerly winter flow and southerly summer flow, so typical to the region. The site is in mountainous terrain of the Alaska Range. The Nenana River flows south to north in a deep canyon. Mountains surround the site in all directions. As a result, the winds do not favor particular directions and no seasonal trends were observed with this data (Appendix C).

4.2.3 Trapper Creek Air Flow

Air flow in the Trapper Creek area is predominately north or south, depending on the season, because of the orientation of the Susitna River valley. Winds were monitored at Trapper Creek from July 1, 1998 to June 30, 2001. During the July to August periods the winds were mixed with directions out of the north or south equally. September was a month of transitioning from equal northerly and southerly winds to mostly northerly. During the Fall/Winter season (October to March), the winds were primarily out of the north. April was a transition month which saw winds begin to switch to southerly. May and June saw the cycle complete with equally mixed northerly and southerly winds (Appendix C).

5.0 CONCLUSIONS

This three-year study has provided insight into the comparability of Denali with two sites, Poker Flat and Trapper Creek, which were chosen to represent the regional conditions. The data collected during this study is available at www2.nature.npsgov/ard/pubs/DENA_report.htm.

The annual variability of the meteorology and chemical component concentrations at the three sites is significantly high. Any further studies must be designed for multiple years to account for this variability.

Analysis of the meteorological data has provided the following information:

- Air flow in the Poker Flat area is very seasonal. During the May to August period the winds were primarily out of the west-southwest to southwest. During the month of September the winds transitioned from west-southwest to east-northeast. During the fall/winter seasons (October – March) the winds were primarily out of the east-northeast. April was a month of transitioning from east-northeast back to west-southwest.
- Air flow in the Denali National Park site is complex. The winds do not favor particular directions and no seasonal trends were observed with this data.
- Air flow in the Trapper Creek area is predominantly north to south, depending on the season. During the May to August periods the winds were mixed with directions out of the north and south equally. September was a month of transitioning to mostly northerly winds. During the fall/winter season (October to March); the winds were primarily out of the north. April was a transition month which saw winds begin to shift to southerly.

Analysis and comparisons of the chemical concentration data has provided several important results:

- Most of the components measured at Denali appear to be regional in nature.
- Sulfate appears to be regional and primarily of the form of ammonium sulfate although periods of ammonium bisulfate occur, especially during winter. Sulfate concentrations are usually highest in the winter/spring (~ 0.1-1.0μg m^{-3}) and lowest in the summer/fall (~ 0.05-0.3μg m^{-3}) seasons. Arctic haze may be responsible for a majority of the sulfate observed during the winter.
- Sulfur dioxide shows the strongest seasonal variability of the components included in this study. During the spring, summer and early fall seasons (April through October); sulfur dioxide concentrations are consistently low at Denali and Poker Flat. During the mid-fall and winter seasons (November through March), sulfur dioxide concentrations are consistently higher than summer values at Denali and Poker Flat.
- The sulfur dioxide concentrations at Trapper Creek remain low (~ 0.1-0.2μg m^{-3}) for the entire three year study.
- During the first two winters, Denali and Poker Flat appear to be influenced by regional sources of sulfur dioxide and during all three winters, there is a source of

sulfur dioxide that causes the Denali concentrations to be above regional background values.

- Particulate nitrate concentrations are generally higher at Trapper Creek than at Poker Flat and Denali, but on average remain low (< 0.1μg m^{-3} for Poker Flat and Denali and < 0.2μg m^{-3} for Trapper Creek).
- Particulate ammonium concentrations are usually low (between 0.02 and 0.2μg m^{-3}). Ammonium reaches its maximum during the spring/summer months when biological activity is high.
- A high degree of variability was seen when comparisons were made for each component between each site. This variability may be attributed to different emission sources, values at or below the minimum detectable limit, or meteorological conditions (wind speed, wind direction, temperature and relative humidity). Good correlations were consistent for the following:
  - Sulfate, between all sites in the summer and winter seasons
  - Nitric acid, between all sites during the spring and summer seasons
  - Ammonium, between all sites during the summer season
- A high degree of variability was also seen when comparisons were made between components at each site. This variability may be attributed to different emission sources, values at or below the minimum detectable limit, or meteorological conditions (wind speed, wind direction, temperature and relative humidity). Sulfate and ammonium demonstrated good correlations for almost all seasons at all sites, with the exception of Poker Flat during Year 1 of the study. Poor correlations were seen for almost all sites during all seasons for: sulfur dioxide and sulfate, ammonium and sulfur dioxide, ammonium and particulate nitrate, and particulate nitrate and nitric acid. The remainder of the between component correlations varied significantly by site and by year.
- Spring and summer of 2000 had a high number of good correlations between many different components, indicating the presence of wildfire smoke.

6.0 ACKNOWLEDGEMENTS

The authors wish to thank:

- T.A. Cahill, University of California-Davis, for his assistance in the preparation of this report.
- The Geophysical Institute of University of Alaska-Fairbanks, for the use of Poker Flat Research Range.
- KTNA, Talkeetna Community Radio, Inc, for use of their transmitter shelter and property.
- Site operators Ray Medbery, Joan Medbery, June Pelehowski, and Brian Lawson, for reliable data collection.

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APPENDIX A

INSTRUMENTATION

Instrumentation Used in the Poker Flat,
Denali National Park and Preserve,
and Trapper Creek Dry Deposition Network

Poker Flat

Instrument	Model
Wind Speed and Direction Sensor	R.M. Young 053505
Temperature Sensor	Campbell Model 107
Filter Pack Mass Flow Controller (MFC)	Tylan FC-280SAV
MFC Read out box	Tylan RO-32
Data Logger	Campbell 21XL
Data Storage Modules	Campbell SM192

Denali National Park and Preserve

Instrument	Model
Wind Speed Sensor	Climatronics F460
Wind Direction Sensor	Climatronics F460
Temperature Sensor	Climatronics
Filter Pack Mass Flow Controller (MFC)	Tylan FC-280SAV
MFC Read out box	Tylan RO-32
Data Logger	SumX SX444

Trapper Creek

Instrument	Model
Wind Speed and Direction Sensor	R.M. Young 053505
Temperature Sensor	Campbell Model 107
Filter Pack Mass Flow Controller (MFC)	Tylan FC-280SAV
MFC Read out box	Tylan RO-32
Data Logger	Campbell 21XL
Data Storage Modules	Campbell SM192

APPENDIX B

BETWEEN SITE CORRELATIONS

Table B-1

Between site correlations (R^2) for specific components, Year 1 (July 1998-June 1999)

Time Period	Poker vs. Denali R^2	Denali vs. Trapper R^2	Poker vs. Trapper R^2
SO_4			
Summer	**0.89**	**0.86**	**0.79**
Fall	0.20	**0.58**	0.08
Winter	**0.73**	**0.53**	**0.61**
Spring	0.17	0.22	0.00
Annual	**0.50**	**0.50**	0.22
Total SO_2			
Summer	**0.53**	0.32	0.38
Fall	**0.63**	0.11	0.00
Winter	**0.60**	**0.65**	0.33
Spring	0.05	0.00	0.11
Annual	**0.64**	0.19	0.27
Particulate NO_3			
Summer	0.02	0.33	0.06
Fall	0.42	0.19	0.08
Winter	**0.91**	0.29	0.26
Spring	0.02	0.03	0.06
Annual	**0.68**	0.18	0.08
HNO_3			
Summer	0.49	**0.65**	0.48
Fall	0.47	0.00	0.16
Winter	0.02	0.22	0.03
Spring	**0.78**	**0.70**	**0.93**
Annual	0.07	0.22	0.32
NH_4			
Summer	**0.80**	**0.79**	**0.74**
Fall	**0.56**	**0.65**	**0.53**
Winter	0.11	0.43	0.04
Spring	**0.54**	0.31	0.26
Annual	0.47	0.46	0.47

*Correlations between components that have an R^2 greater than 0.5 are in bold type.
**These correlations are presented visually in Figures 4-9, 4-13, 4-17, 4-21, and 4-15.

Table B-2

Between site correlations (R^2) for specific components, Year 2 (July 1999-June 2000)

Time Period	Poker vs. Denali R^2	Denali vs. Trapper R^2	Poker vs. Trapper R^2
SO_4			
Summer	**0.54**	**0.65**	**0.64**
Fall	0.42	0.00	0.02
Winter	**0.72**	**0.70**	0.46
Spring	**0.89**	**0.61**	0.37
Annual	**0.78**	**0.52**	0.38
Total SO_2			
Summer	0.00	0.00	0.04
Fall	0.15	**0.58**	0.02
Winter	0.03	**0.62**	0.34
Spring	0.01	0.30	0.05
Annual	0.23	0.33	0.09
Particulate NO_3			
Summer	0.05	0.06	**0.57**
Fall	**0.93**	0.04	0.06
Winter	**0.62**	0.35	0.32
Spring	0.00	0.11	0.04
Annual	0.34	0.07	0.12
HNO_3			
Summer	**0.65**	**0.53**	**0.83**
Fall	0.00	0.02	0.03
Winter	0.06	0.03	0.05
Spring	**0.69**	**0.62**	0.32
Annual	0.22	0.35	0.25
NH_4			
Summer	**0.57**	**0.57**	0.45
Fall	0.06	0.14	0.13
Winter	**0.77**	**0.72**	0.44
Spring	**0.84**	0.35	0.13
Annual	**0.80**	**0.55**	0.35

*Correlations between components that have an R^2 greater than 0.5 are in bold type.
**These correlations are presented visually in Figures 4-10, 4-14, 4-18, 4-22, and 4-26.

Table B-3

Between site correlations (R^2) for specific components, Year 3 (July 2000-June 2001)

Time Period	Poker vs. Denali R^2	Denali vs. Trapper R^2	Poker vs. Trapper R^2
SO_4			
Summer	**0.77**	0.48	**0.61**
Fall	0.00	0.18	0.01
Winter	**0.85**	**0.86**	**0.83**
Spring	0.06	0.19	0.09
Annual	**0.54**	**0.60**	**0.63**
Total SO_2			
Summer	0.01	0.08	0.31
Fall	0.00	0.18	0.00
Winter	0.23	0.21	0.18
Spring	0.02	0.06	0.26
Annual	0.24	0.30	0.25
Particulate NO_3			
Summer	**0.85**	**0.52**	**0.60**
Fall	0.10	0.06	0.02
Winter	0.05	0.46	0.20
Spring	**0.56**	0.29	0.31
Annual	0.39	0.29	0.22
HNO_3			
Summer	**0.98**	**0.65**	**0.70**
Fall	0.00	0.00	0.02
Winter	0.00	**0.50**	0.39
Spring	0.09	**0.74**	0.22
Annual	0.29	**0.66**	0.31
NH_4			
Summer	**0.91**	**0.64**	**0.74**
Fall	0.00	0.40	0.10
Winter	**0.88**	**0.77**	**0.70**
Spring	0.21	0.20	0.40
Annual	**0.61**	**0.57**	**0.61**

*Correlations between components that have an R^2 greater than 0.5 are in bold type.
**These correlations are presented visually in Figures 4-11, 4-15, 4-19, 4-23, and 4-27.

Table B-4

Between site correlations (R^2) for specific components, All Years (July 1998-June 2001)

Time Period	Poker vs. Denali R^2	Denali vs. Trapper R^2	Poker vs. Trapper R^2
SO_4			
Summer	**0.60**	**0.61**	**0.62**
Fall	0.33	0.14	0.08
Winter	**0.73**	**0.68**	**0.51**
Spring	0.40	0.36	0.19
Annual	**0.64**	**0.57**	0.45
Total SO_2			
Summer	0.06	0.07	0.10
Fall	**0.55**	0.12	0.09
Winter	0.38	0.49	0.35
Spring	0.00	0.03	0.14
Annual	0.49	0.25	0.25
Particulate NO_3			
Summer	0.24	0.22	0.35
Fall	**0.58**	0.03	0.07
Winter	**0.80**	0.39	0.33
Spring	0.11	0.10	0.03
Annual	**0.51**	0.16	0.10
HNO_3			
Summer	**0.70**	0.41	**0.67**
Fall	0.03	0.09	0.31
Winter	0.00	0.04	0.07
Spring	0.44	**0.71**	0.38
Annual	0.20	0.34	0.30
NH_4			
Summer	**0.71**	**0.58**	**0.52**
Fall	0.43	0.49	0.43
Winter	**0.50**	**0.57**	0.28
Spring	0.44	0.29	0.12
Annual	**0.61**	**0.57**	0.41

*Correlations between components that have an R^2 greater than 0.5 are in bold type.
**These correlations are presented visually in Figures 4-8, 4-12, 4-16, 4-20, and 4-24.

APPENDIX C

WIND ROSES

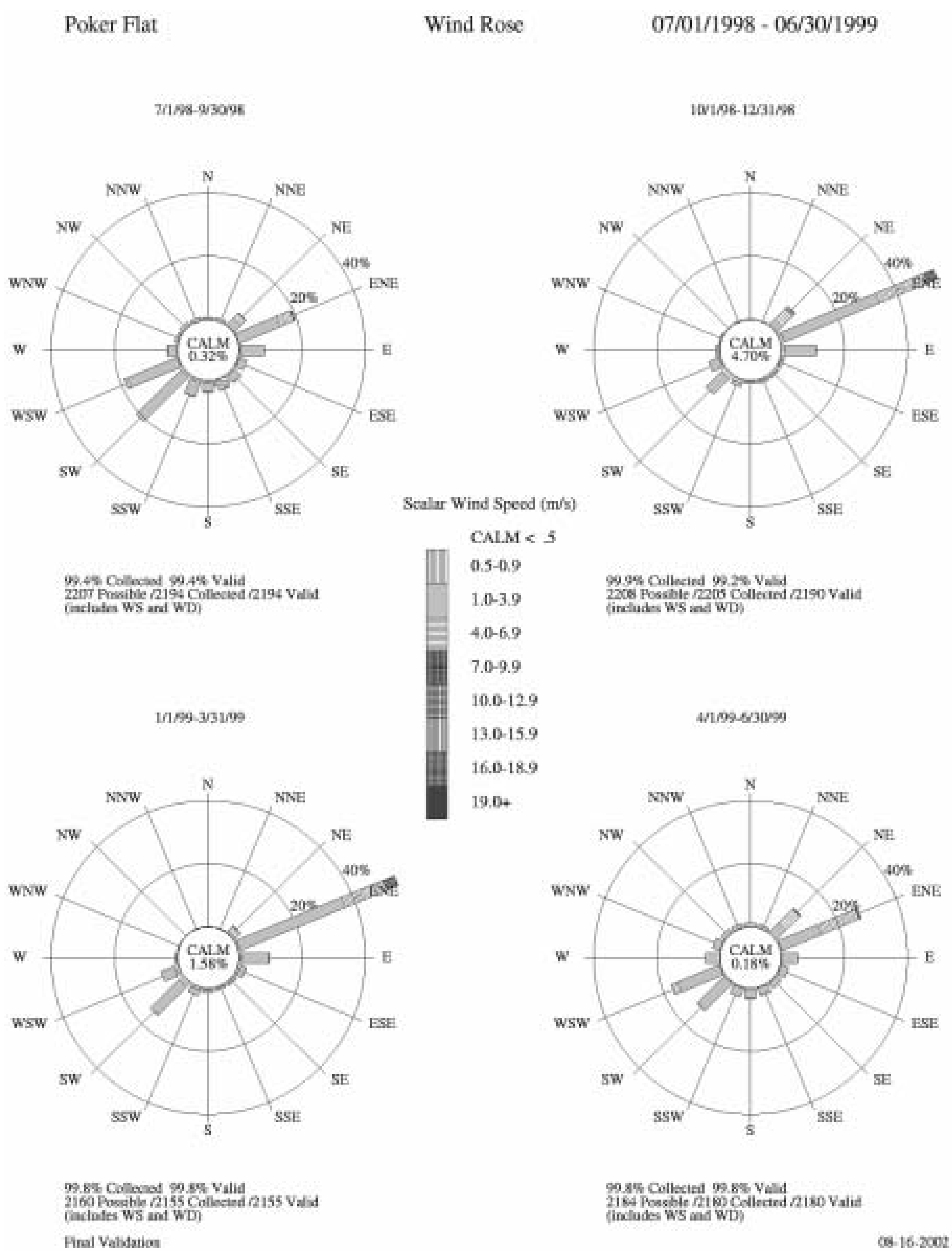

Figure C-1. Poker Flat Quarterly Wind Rose, 1998-1999.

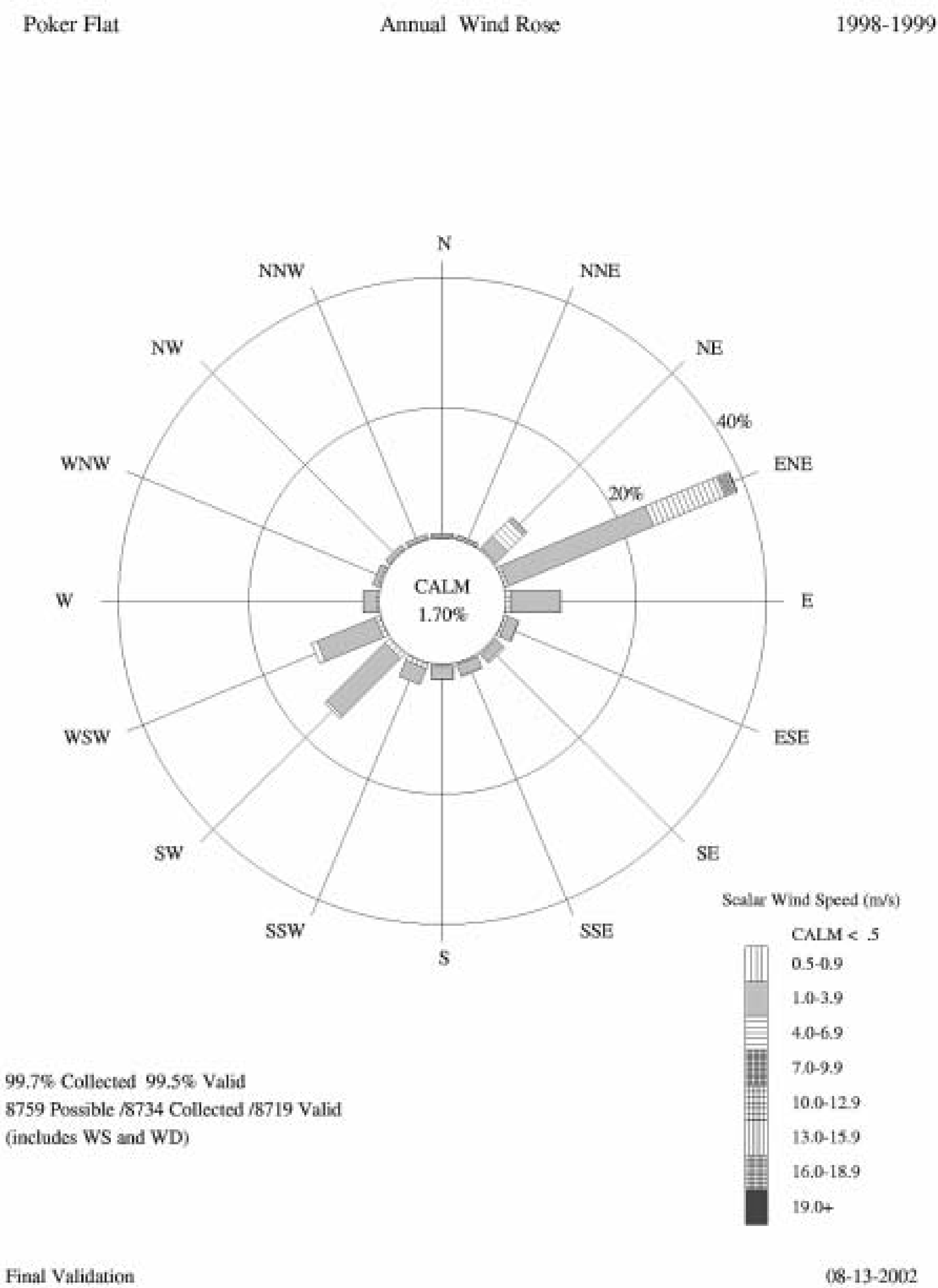

Figure C-2. Poker Flat Annual Wind Rose, 1998-1999.

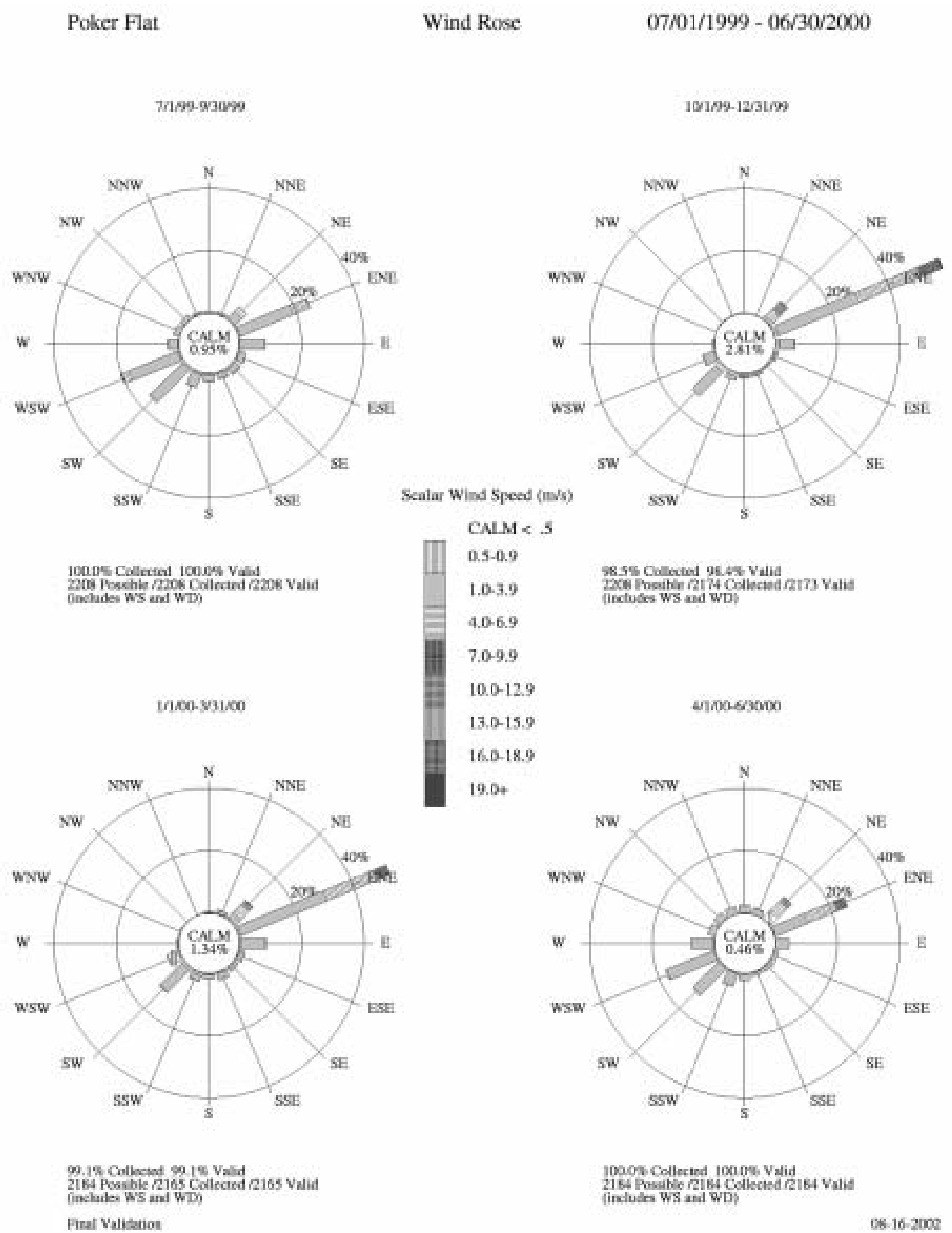

Figure C-3. Poker Flat Quarterly Wind Rose, 1999-2000.

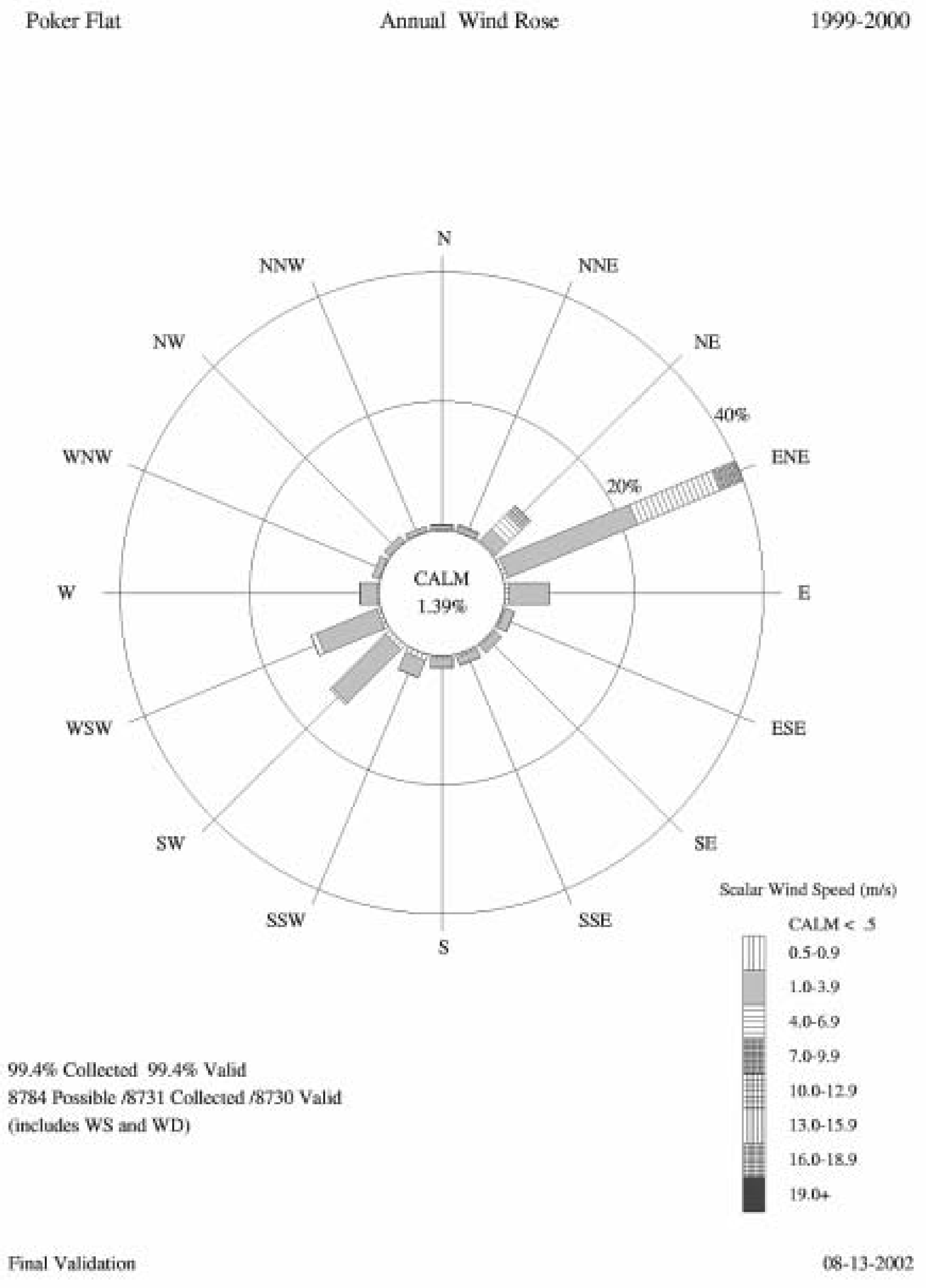

Figure C-4. Poker Flat Annual Wind Rose, 1999-2000.

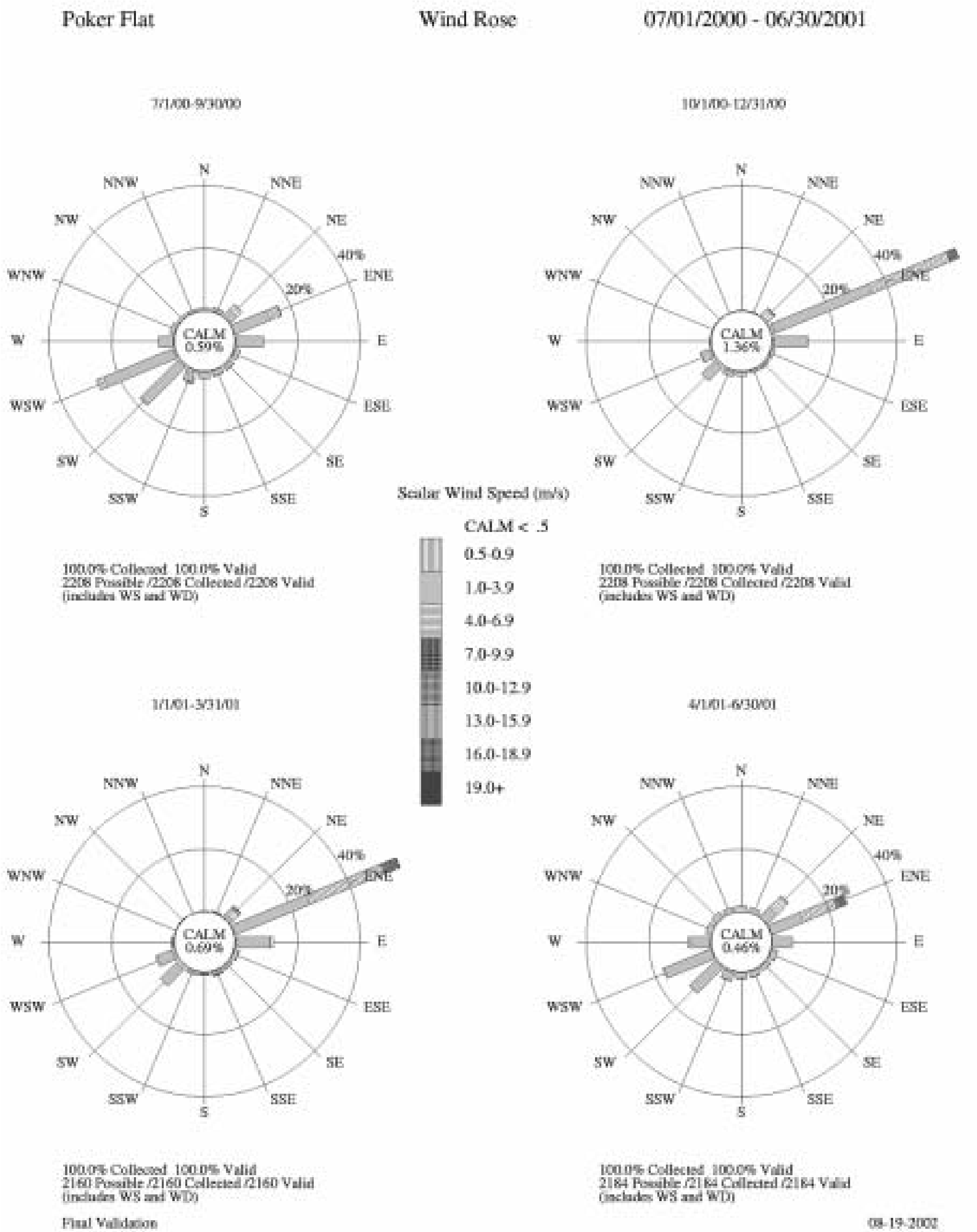

Figure C-5. Poker Flat Quarterly Wind Rose, 2000-2001.

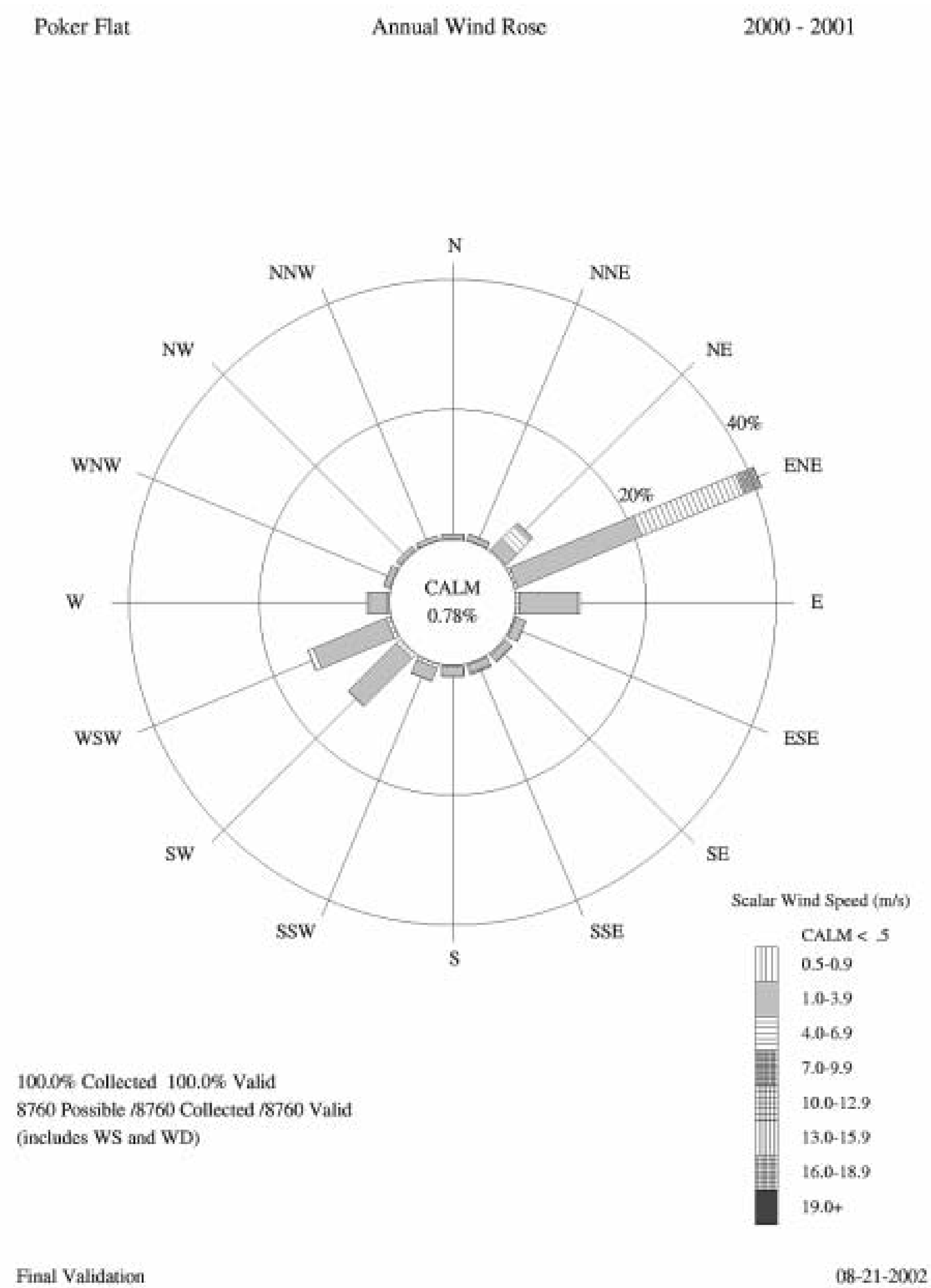

Figure C-6. Poker Flat Annual Wind Rose, 2000-2001.

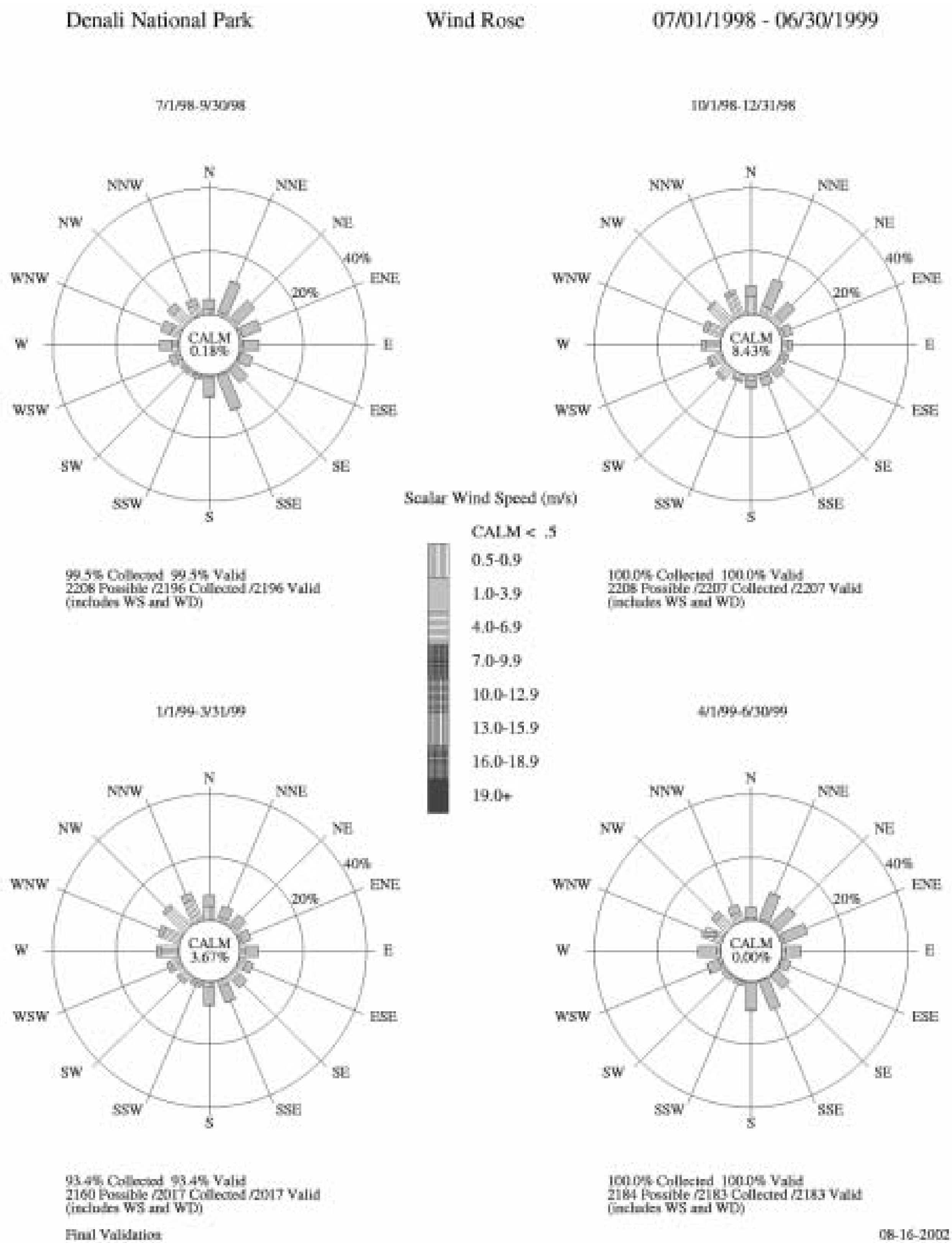

Figure C-7. Denali National Park Quarterly Wind Rose, 1998-1999.

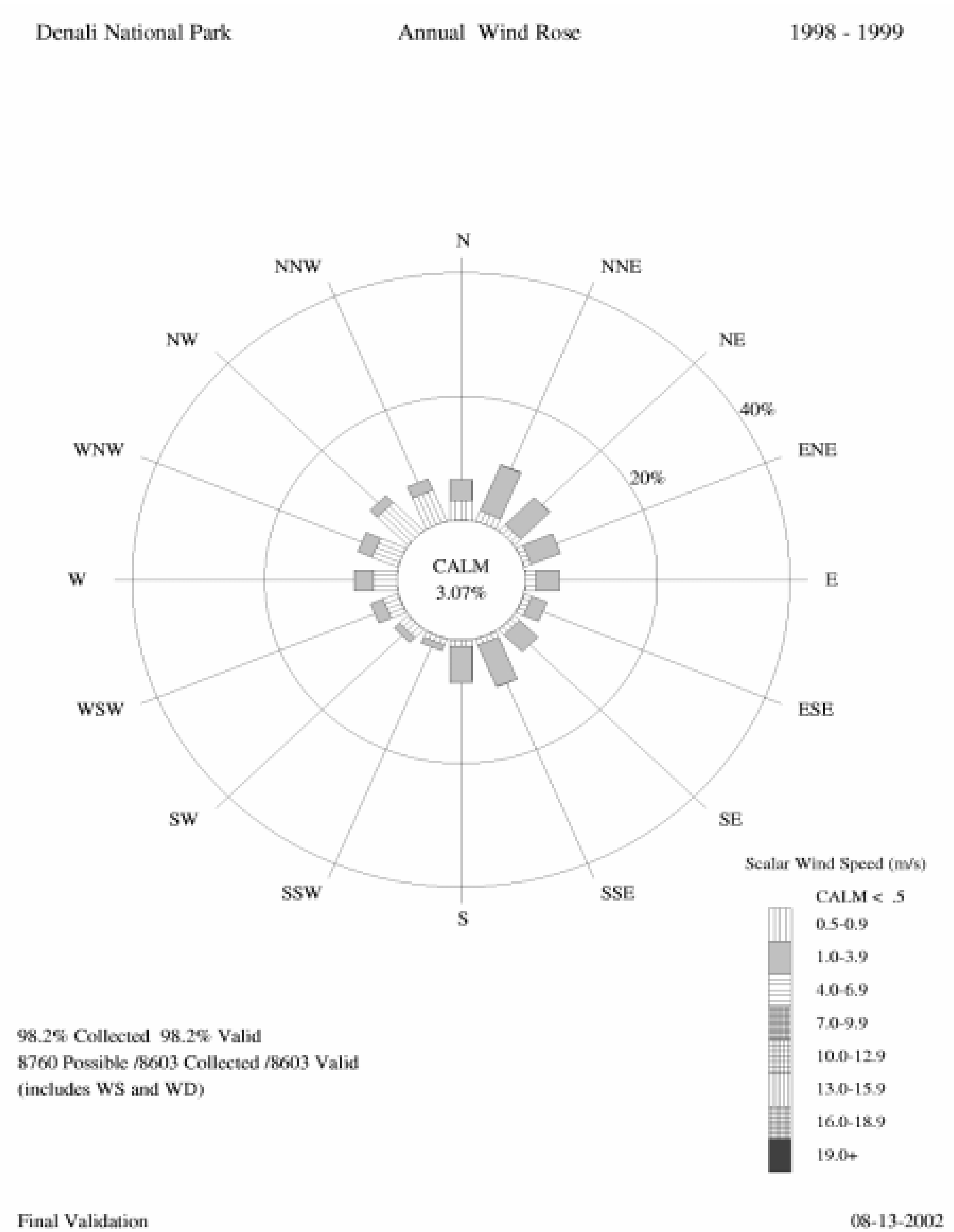

Figure C-8. Denali National Park Annual Wind Rose, 1998-1999.

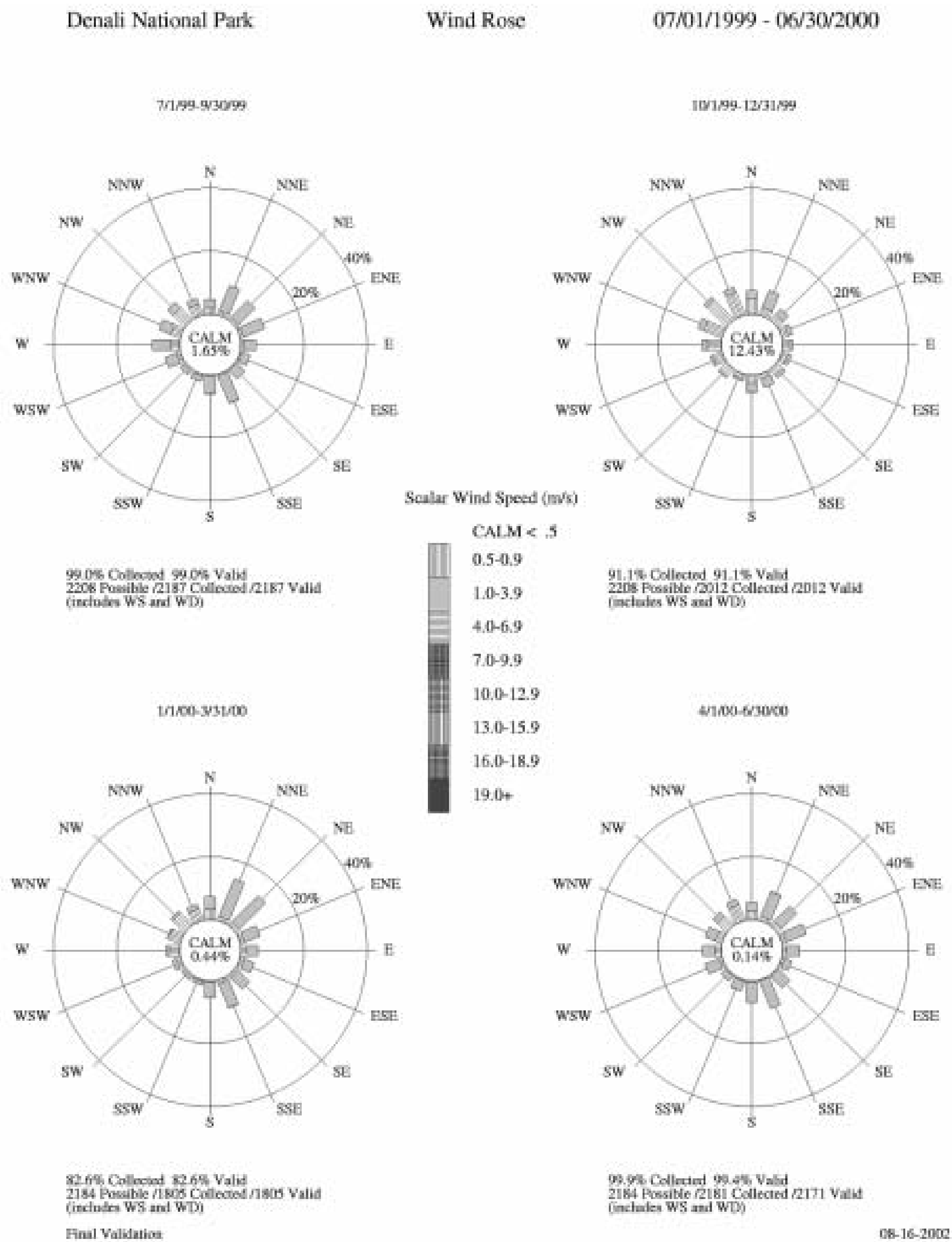

Figure C-9. Denali National Park Quarterly Wind Rose, 1999-2000.

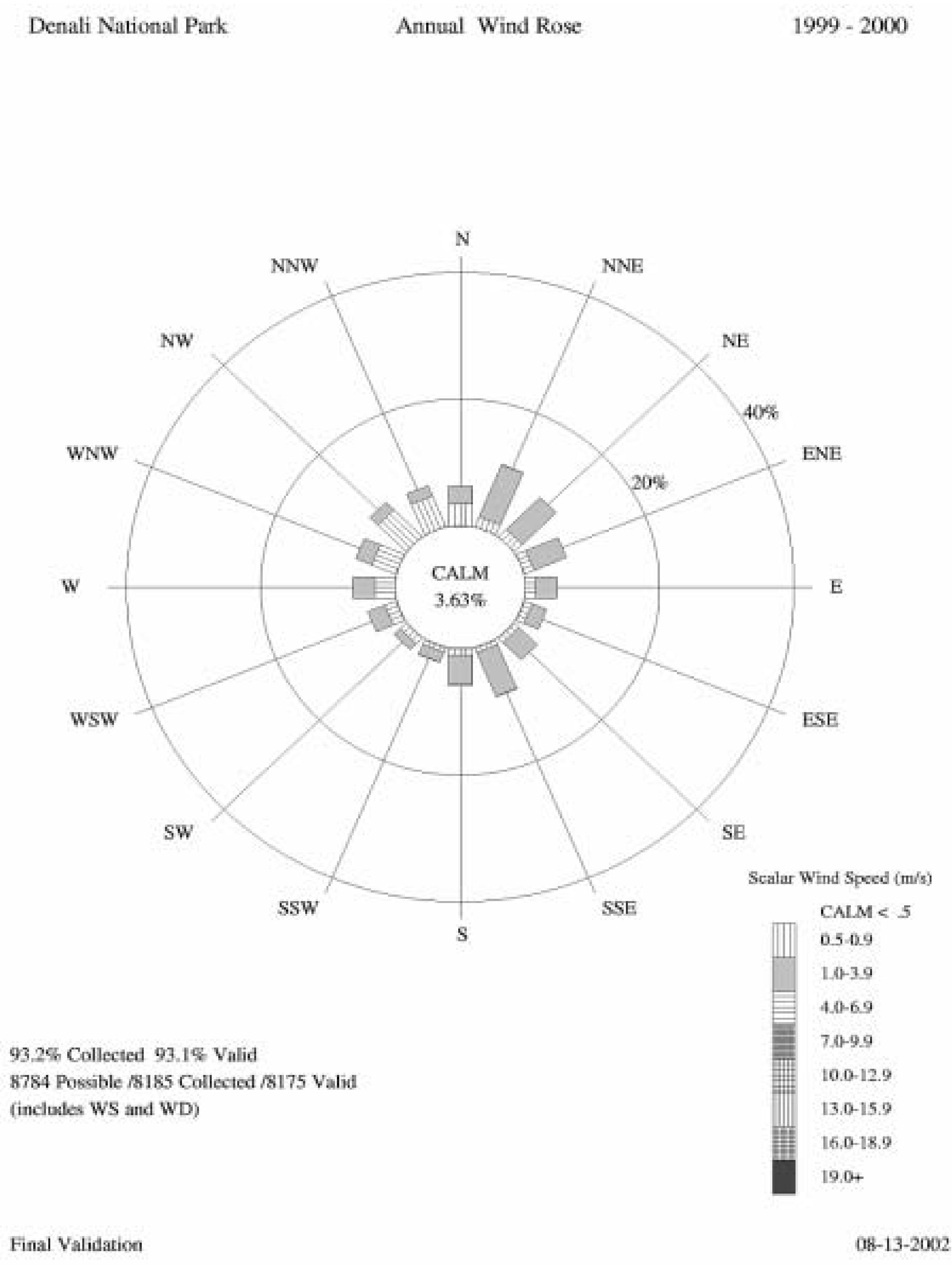

Figure C-10. Denali National Park Annual Wind Rose, 1999-2000.

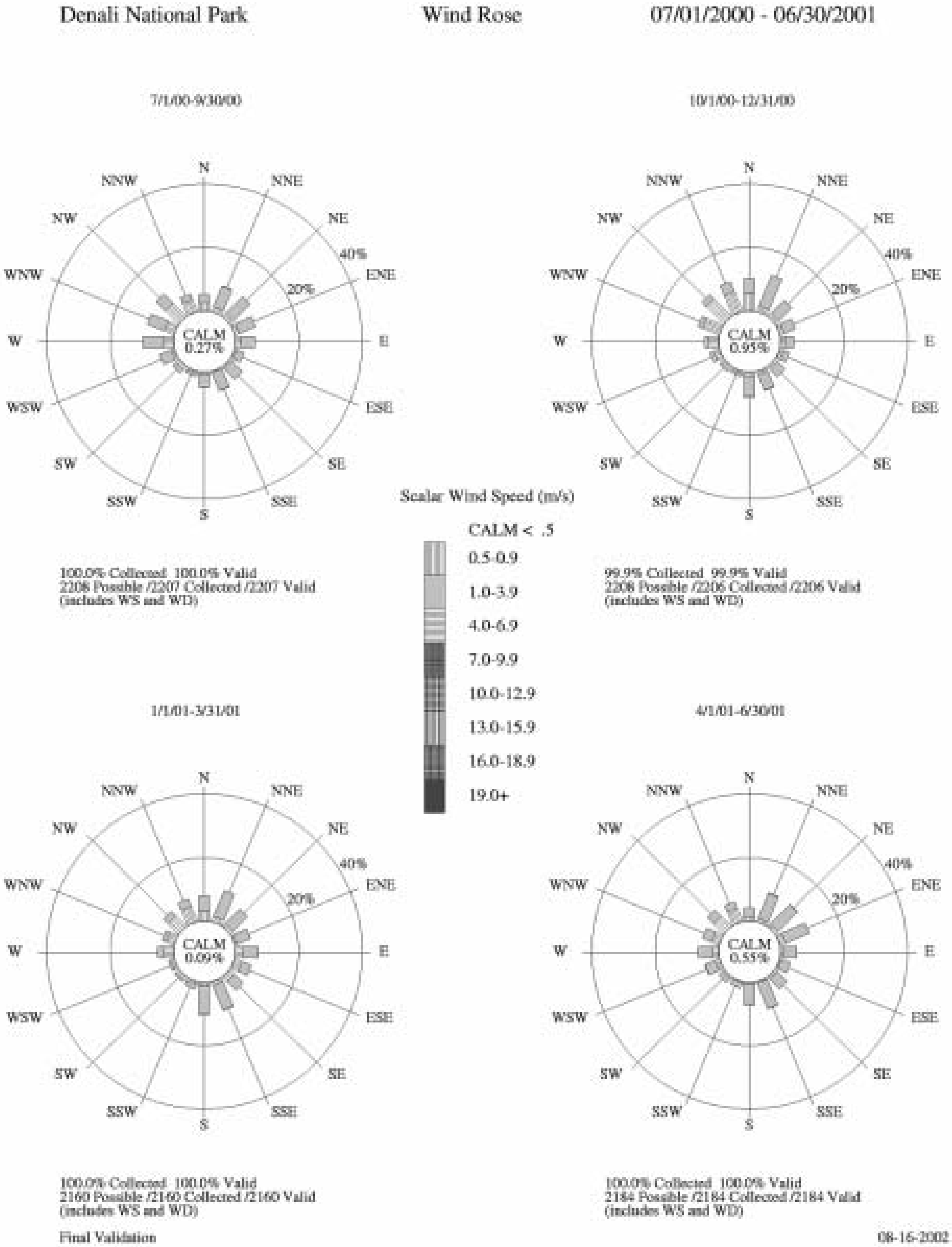

Figure C-11. Denali National Park Quarterly Wind Rose, 2000-2001.

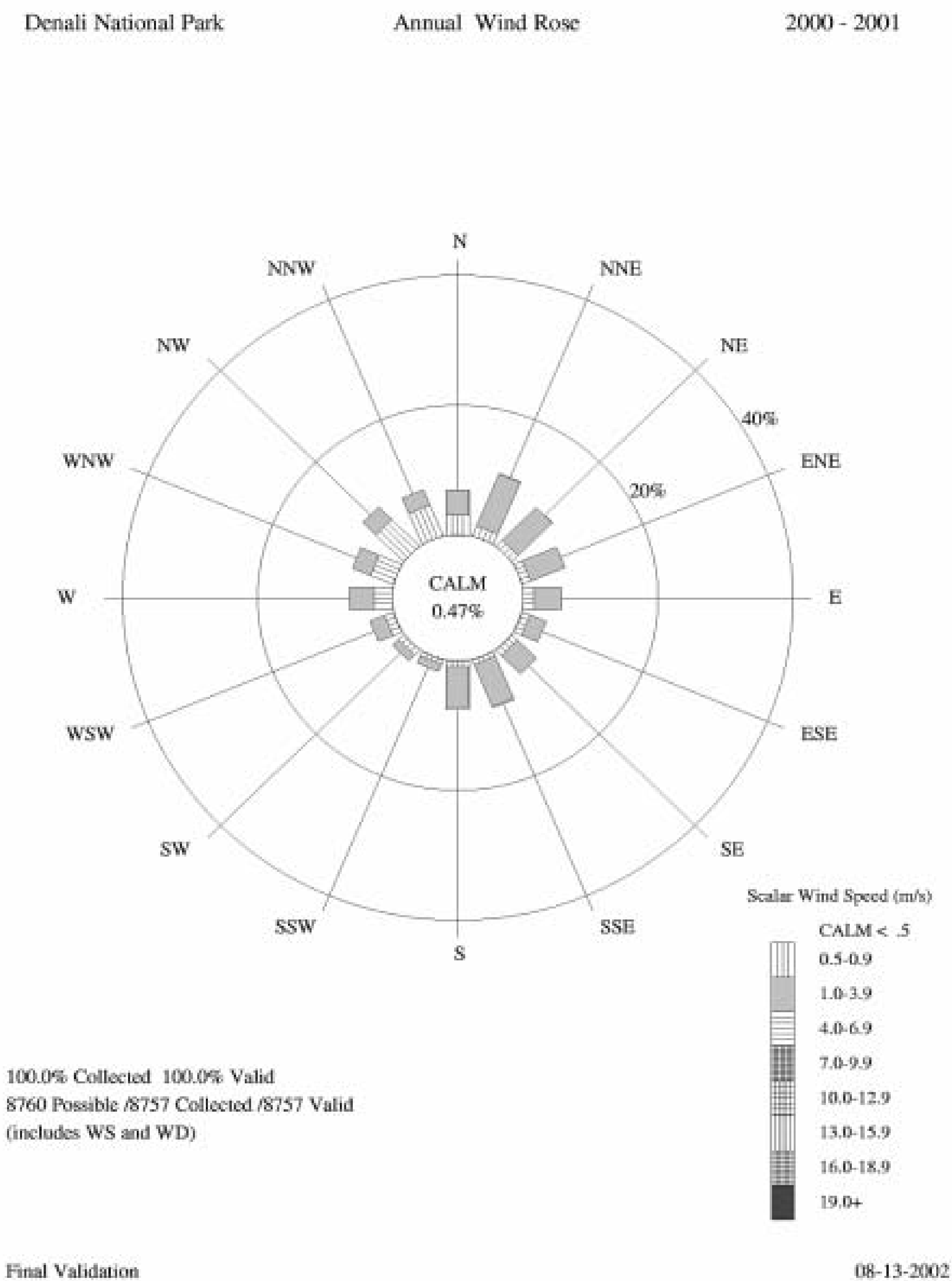

Figure C-12. Denali National Park Annual Wind Rose, 2000-2001.

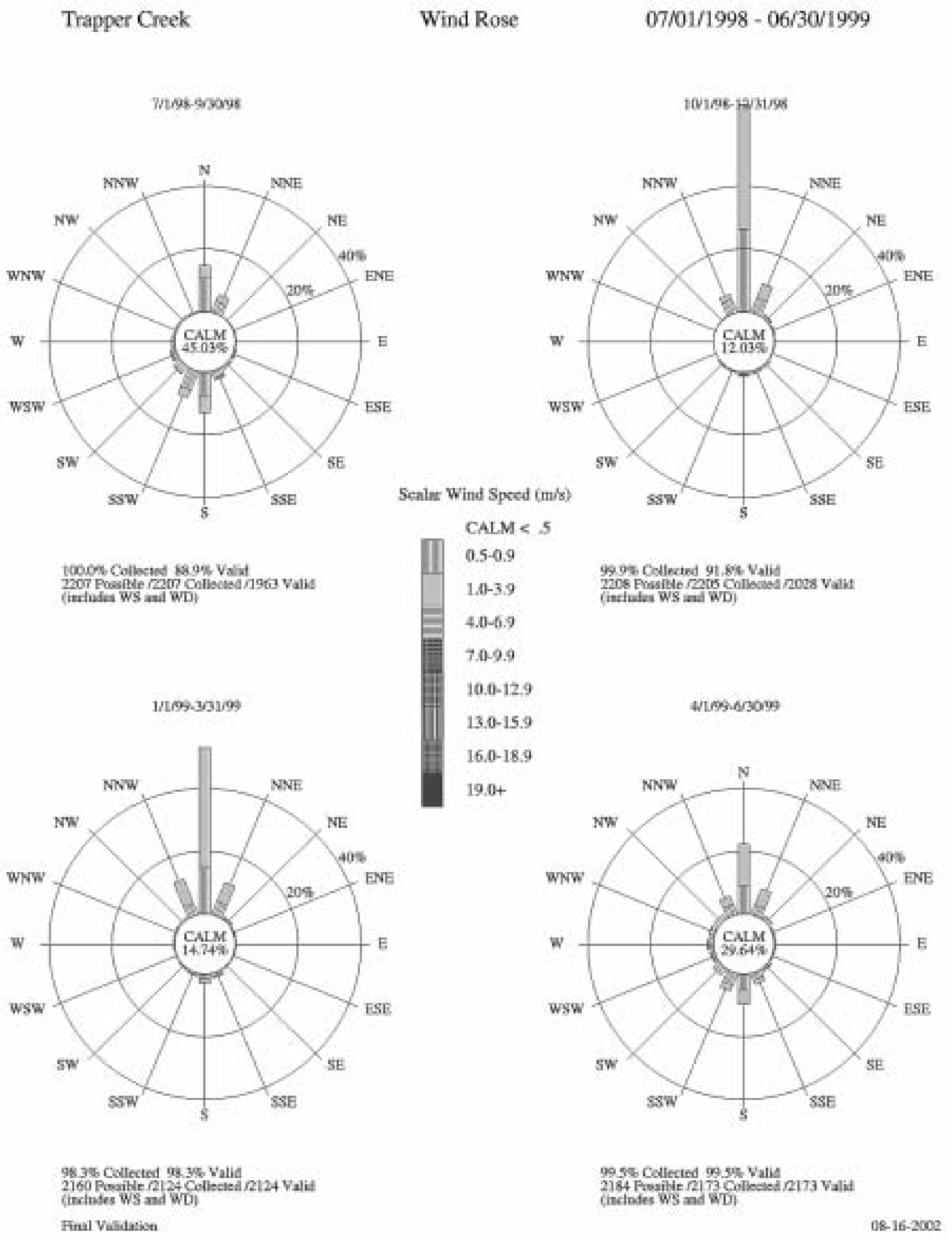

Figure C-13. Trapper Creek Quarterly Wind Rose, 1998-1999.

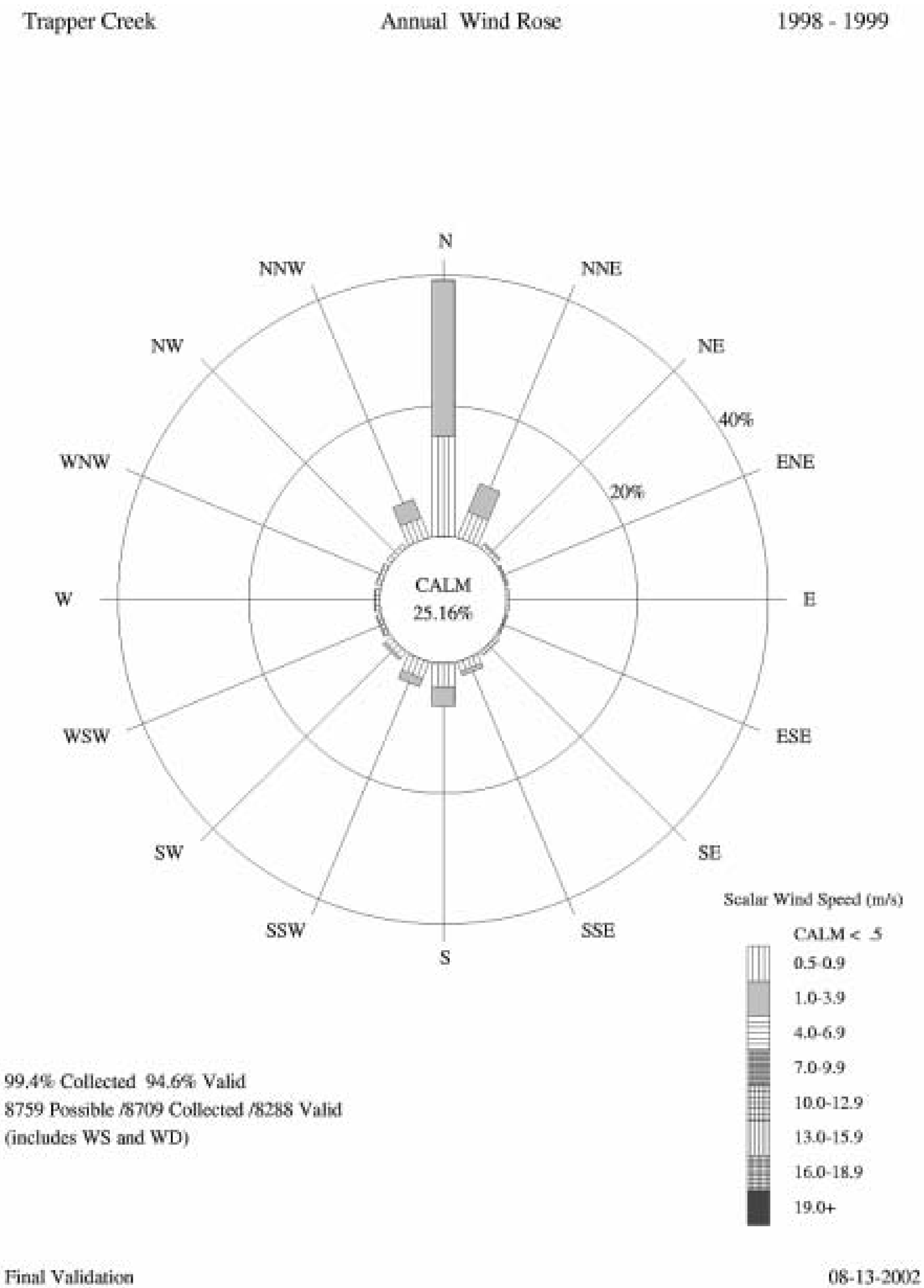

Figure C-14. Trapper Creek Annual Wind Rose, 1998-1999.

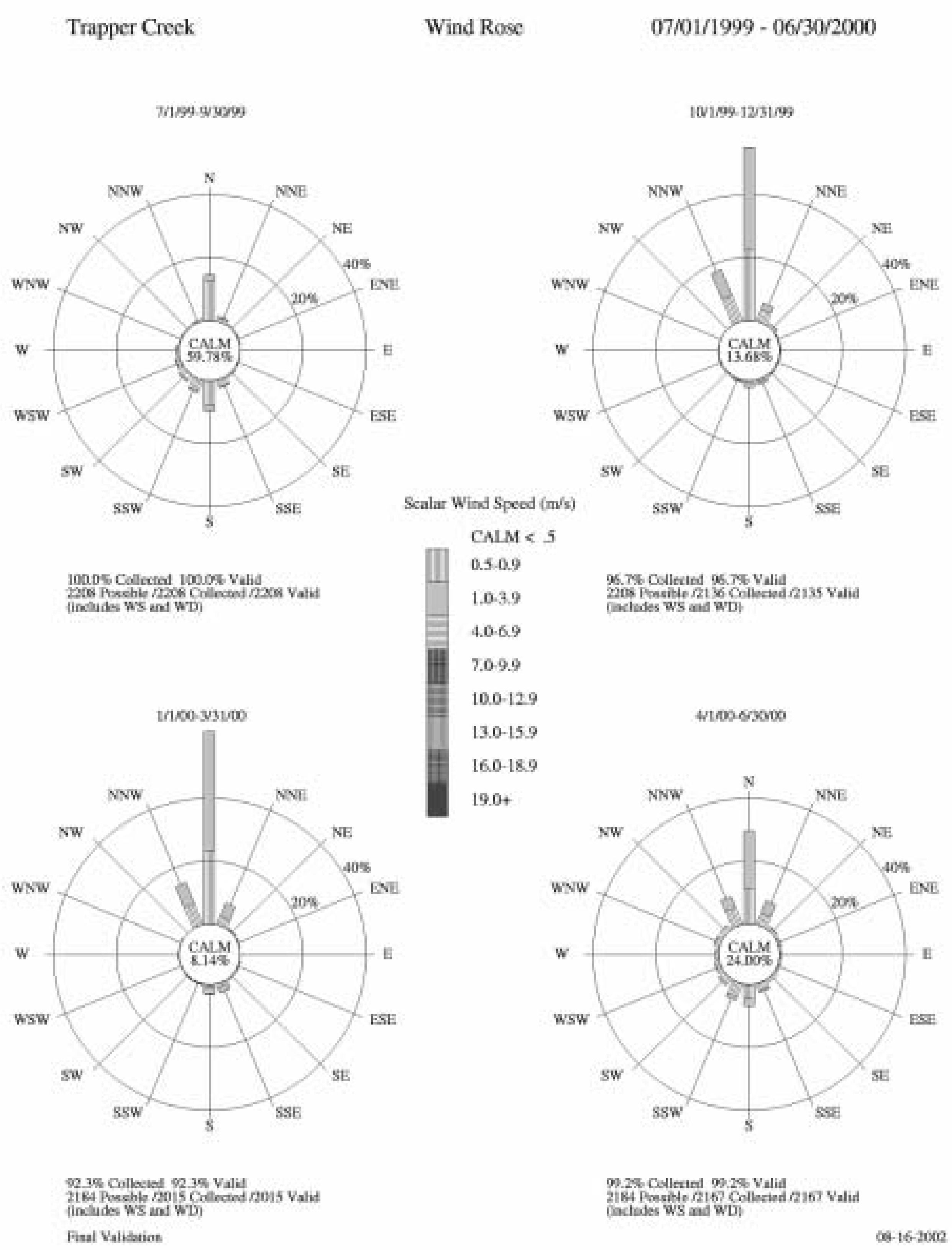

Figure C-15. Trapper Creek Quarterly Wind Rose, 1999-2000.

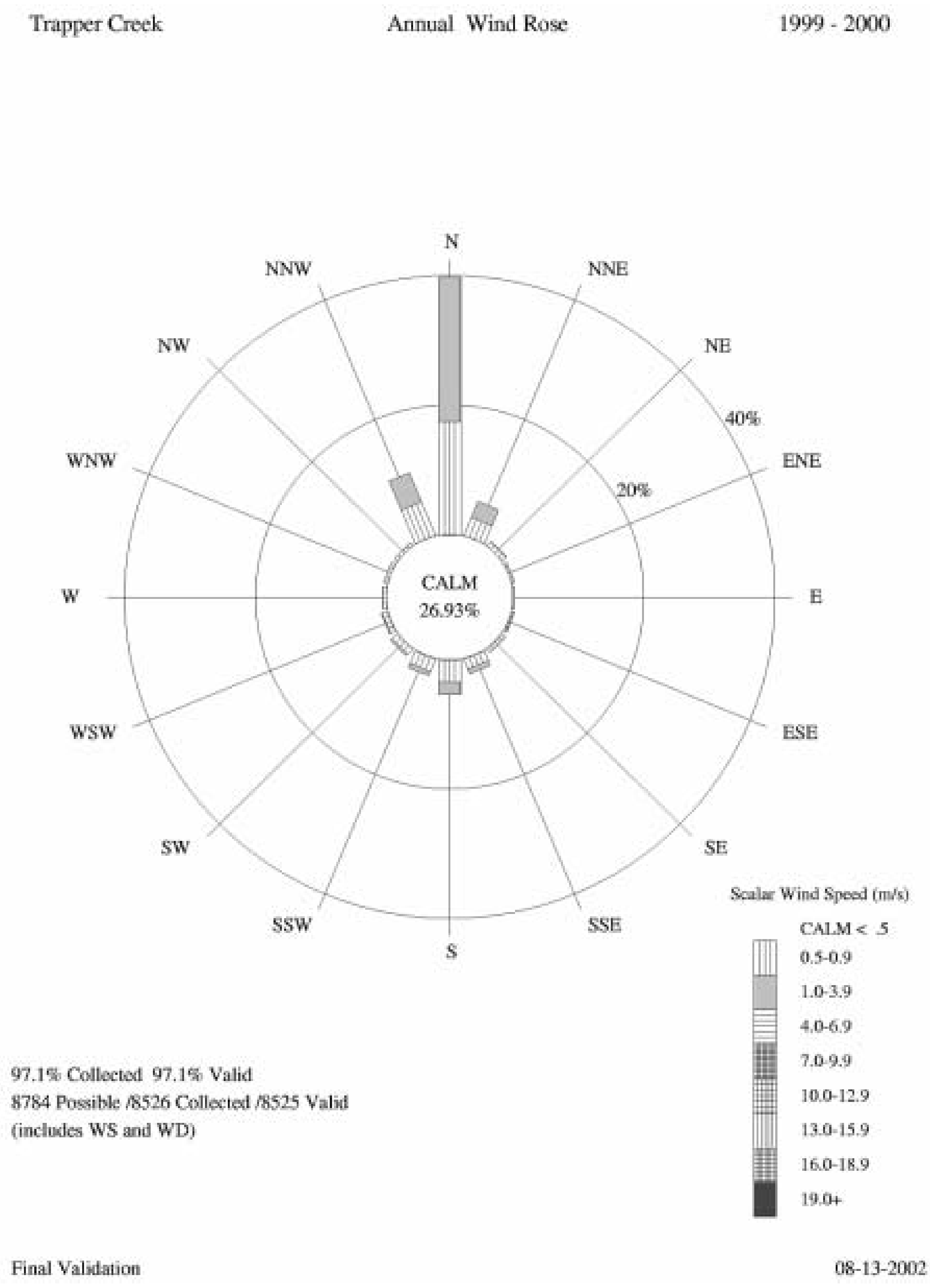

Figure C-16. Trapper Creek Annual Wind Rose, 1999-2000.

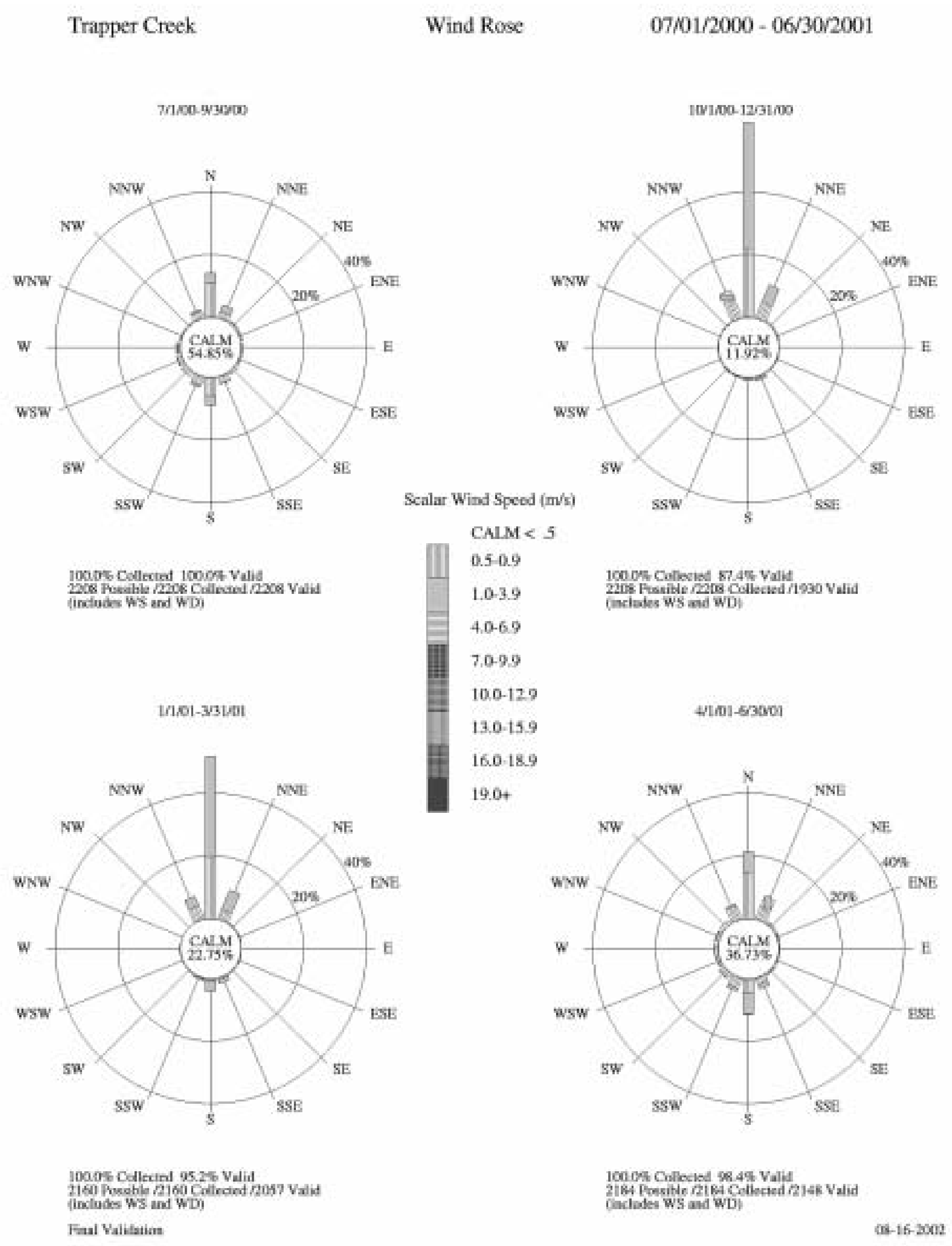

Figure C-17. Trapper Creek Quarterly Wind Rose, 2000-2001.

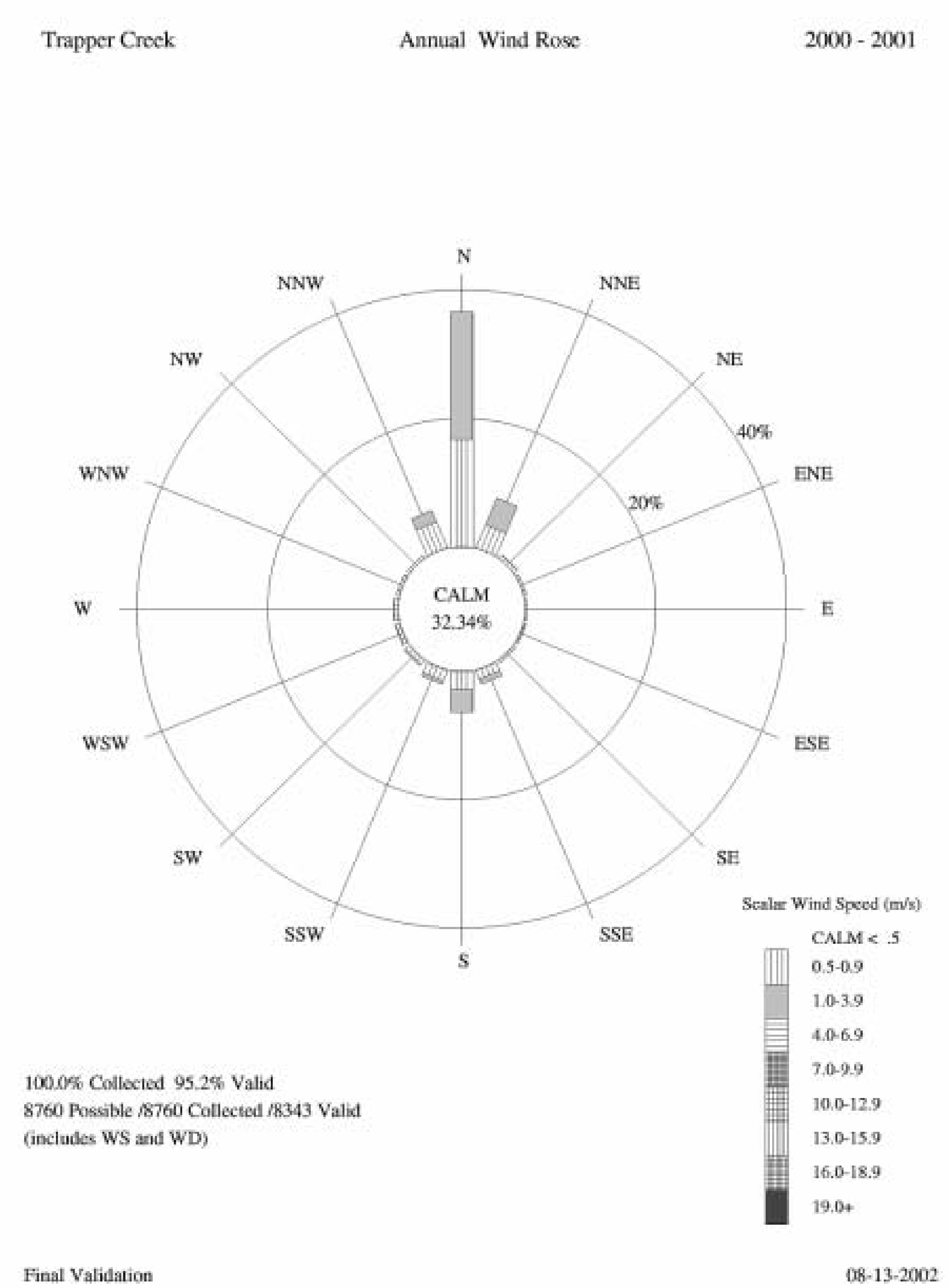

Figure C-18. Trapper Creek Annual Wind Rose, 2000-2001.